COORDINATION CATALYSIS

Studies on the fixation of metal complexes and on the olefin metathesis reaction

MATS BERGLUND

Lund 1986

COORDINATION CATALYSIS

Studies on the fixation
of metal complexes and on
the olefin metathesis reaction

AVHANDLING FÖR FILOSOFIE DOKTORSEXAMEN

Avhandlingen kommer att försvaras vid offentlig
disputation å Kemicentrum, hörsal D,
tisdagen den 27 maj, kl 10.15

av

Mats Berglund
HE., Klr

Digitized by the Internet Archive
in 2026

https://archive.org/details/IA41546727_0054

COORDINATION CATALYSIS

Studies on the fixation of metal complexes and on the olefin metathesis reaction

MATS BERGLUND

Lund 1986

Berglund, M. (1986)

Thesis. Inorganic Chemistry 1, Chemical Center,
University of Lund, P.O.B. 124
S-221 00 LUND, SWEDEN.

Organization	Document name
LUND UNIVERSITY	DOCTORAL DISSERTATION
Inorganic Chemistry 1 Chemical Center P.O.B 124, S-22100 Lund, SWEDEN	Date of issue: May 1986 CODEN: LUNKDL/(NKOO-1010)/001-033/1986
Author(s): Mats Berglund	Sponsoring organization

Title and subtitle: COORDINATION CATALYSIS
Studies on the fixation of metal complexes and on the olefin metathesis reaction.

Abstract

Two methods for the preparation of the silica-bound chelating phosphine ligand bis(diphenylphosphino)maleimide are descriebed. In the first a aminated silica surface is treated with bis(diphenylphosphino)maleic-acidanhydride. By use of different Group VI carbonyl complexes as IR-probes it is shown that this method yields two different metal-binding sites viz. amine and bisphosphine groups. In the second method the condensation between the anhydride and the amine was performed in solution and the thus formed maleimide was linked without prior isolation to the silica surface. Use of the same type of IR-probes as above shows that only bisphosphine groups are present on the surface.

The metathesis of Z-2-pentene has been studied using $Mo(NO)_2L_2Cl_2$ immobilized on a polar organic polymer viz. a copolymer of hydroxyethyldimethacrylate and ethylendimethacrylate, as the catalyst. The co-catalyst was found to interact with polar functional groups on the polymer. The reaction of ester groups wih $EtAlCl_2$ was mimiced in a study where $Mo(NO)_2(PPh_3)_2Cl_2$ was used as catalyst in the presence of methylstearate.

The cross-metathesis of various alkenylsilanes viz. $CH_2=CH(CH_2)_nSiX_3$ (n=0-2, X=Cl,OMe,Me) and Z-2-pentene, have been studied using WCl_6-based catalyst systems. The yield of cross-products was found to be dependent on the distance between the double bond and the functional group. For allyltrimethylsilane (ATMS) the reaction proceeds without added co-catalyst but with an induction period. The effect of Lewis acid e.g. AlX_3 (X=Cl,Br) shows that for ATMS, the induction period is completely reduced and the activity substancially increased. The initial activity and the E/Z-stereoselectivity responds similar to the addition of Lewis acid. The result indicate that the Lewis acid infer in the initiating, propagating and terminating step of the reaction.

enl SIS 61 41 21

Key words

Classification system and/or index terms (if any)

Supplementary bibliographical information

Language: English

ISSN and key title

ISBN

Recipient's notes

Number of pages: 105

Price

Security classification

Distribution by (name and address) Mats Berglund, Inorganic Chemistry 1,Chemical Center, P.O.B 124,S-221 00 LUND, Sweden

I, the undersigned, being the copyright owner of the abstract of the above-mentioned dissertation, hereby grant to all reference sources permission to publish and disseminate the abstract of the above-mentioned dissertation.

Signature _____ Date 1986-04-04

COORDINATION CATALYSIS

Studies on the fixation of metal complexes and on the olefin metathesis reaction.

Mats Berglund, Division of Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 124, S-221 00 LUND, Sweden

The thesis consists of this summary and the following papers, referred to in the text by their Roman numerals:

I. Chelating phosphines on silica gel. I. Carbonyl complexes as a mean to probe chelating ligand sites.
M. Berglund, C. Andersson and R. Larsson
J. Organomet. Chem., 258 (1983) 195

II. Hydrogenation of soybean oil with cationic Rh(I)-phosphine complexes as catalysts - para-toluene sulfonate and sulfonated styrene resins as counterions.
M. Berglund and C. Andersson
J. Am. Oil Chem. Soc., 61 (1984) 1351

III. Polar organic polymer as catalyst support in the olefin metathesis reaction.
M. Berglund and C. Andersson
Accepted for publication in J. Mol. Catal.

IV. Olefin metathesis of alkenyltrimethylsilanes.
M. Berglund, C. Andersson and R. Larsson
J. Organomet. Chem., 292 (1985) C15.

V. Olefin metathesis of alkenylsilanes. Part II. On the initiation of the olefin metathesis reaction with organosilanes.
M. Berglund, C. Andersson and R. Larsson
Submitted for publication in J. Organomet. Chem.

CONTENTS

		page
A.	PREFACE	2
B.	FIXATION OF METAL COMPLEXES	3
B 1.	Introduction	3
B 2.	The support	4
B 3.	Methods of characterization	4
B 4.	Synthesis of silica-bound ligands	5
B 5.	Synthesis of silica-bound chelating ligands	7
B 6.	Synthesis of ligands bound to organic polymers	9
B 7.	Fixation of metal complexes	10
B 8.	Immobilization of metal complexes on ion-exchangers	11
C.	OLEFIN METATHESIS	13
C 1.	Introduction	13
	Reaction types	13
C 2.	The carbene mechanism	14
C 3.	Catalyst systems	15
C 3:1.	WCl_6-based systems	16
C 3:2.	The catalyst system WCl_6/allyltrimethylsilane	17
	The induction period	18
	Activity	18
C 3:3.	Catalyst systems based on molybdenum nitrosyl complexes	19
C 3:4.	Reaction conditions	19
C 4.	Polymer-bound metathesis catalyst systems	20
	Olefin metathesis by polymer bound molybdenum nitrosyl complexes	21
C 5.	Metathesis of functionalized olefins	21
C 6.	Metathesis of alkenylsilanes	23
D.	ACKNOWLEDGEMENTS	27
E.	REFERENCES	28

A. PREFACE

One of the most significant developments in the field of catalysis during the past decade has been the discovery and elucidation of the olefin metathesis reaction catalyzed by coordination compounds. This remarkable reaction, as will be discussed further in part C, has greatly stimulated research in a broad field of chemistry e.g. inorganic, organic and polymer chemistry.

Despite the great usefulness and versatility of this reaction and other related olefin conversion reactions rather few homogeneous catalysts have been utilized on an industrial scale. This is because of the technological problems of separation and reuse of the catalyst that are associated with homogeneous systems. To make homogeneous catalyst in general more applicable to industrial processes a new decipline in catalysis appeared in the beginning of the seventies. The general idea is to bind the transition metal complex to a solid support and thereby create a heterogeneous system. This topic is more fully discussed in part B. In the present thesis work from these two fields viz. olefin metathesis and fixation of metal complexes are presented. These two fields are intimately interrelated. A breakthrough in the field of homogeneously catalyzed olefin metathesis can perhaps not be fully exploited until the technique of handling coordination catalysts has been developed.

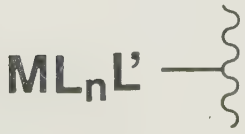
B. FIXATION OF METAL COMPLEXES

B 1. Introduction

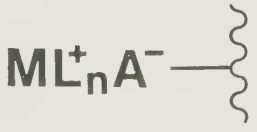
The last twenty years intensive activities in the field of organometallic chemistry have resulted in a great number of homogeneous catalyzed processes. One important starting-point of this development was the discovery of Wilkinson that the rhodium complex $RhCl(PPh_3)_3$ was active as a catalyst for the hydrogenation of olefins [1]. Homogeneous catalysts are often characterized by their high activity under mild conditions and their high selectivity. Alteration of the steric and electronic properties via variation of the ligands makes it possible to tailor-make a catalyst for a specific purpose. For instance, by the use of chiral ligands bound to coordination catalysts it has been possible to transform prochiral substrates to optically active products with high selectivity [2]. These properties makes homogeneous catalysts in many cases superior to the traditional heterogeneous catalysts. However, there is an important difference between homogeneous and heterogeneous catalyst systems since the latter ones can be easily separated from the reaction medium and reused. One way to overcome this problem is to bind the soluble metal complexes to a solid support and thereby create a heterogeneous system. In order to prevent metal leakage the bond between the metal complex and the support must be stable under the reaction conditions. Moreover the immobilization procedure should not alter the properties of the metal complexes. Depending on the type of metal complexes this can be done in two different ways:

a) Immobilization via covalent bonding to a matrix-bound ligand (eq 1).

b) Immobilization via ionic bonding to a matrix-bound counter-ion (eq 2).



Eq.1



Eq.2

Both these methods have been shown to be useful in the synthesis of a great number of matrix-bound metal complexes [3]. In the present thesis method a) is exemplified in papers I and III, method b) in paper II.

B 2. The support

Both organic and inorganic polymers have been used as carriers for immobilized metal complexes [3,21]. The work has mainly concerned commercially available support materials e.g. polystyrene and silica gel. The most important requirements on the supports are that they should be stable (chemically, thermally and mechanically) over a wide range of reaction conditions and have a negligible solubility in the reaction medium.

One very important step in the synthesis of immobilized metal complexes is the functionalization of the support. To enable such an operation the support must have groups on the surface that can be chemically modified. They will act as sites for the introduction of metal-binding groups. In the case of polystyrene, e.g. the phenyl groups, can be functionalized with ordinary methods of organic chemistry. Besides the above mentioned commonly used support materials a great number of potentially useful polymers exists which meet the requirements discussed above. One such example is a strongly cross linked hydroxyethylmethacrylate polymer. The functionalization and subsequent application of this polymer as carrier for some olefin metathesis catalysts are described in paper III.

B 3. Methods of characterization

One problem in the investigation of heterogenized catalyst systems is the complete characterization of the metal complexes. Such studies are, however, essential for the development of suitable synthetic methods.

The use of spectroscopic and many other methods for characterization of immobilized groups are often made difficult by the low concentration of these groups on the support. If the metal

complex contains ligands which strongly absorb light in the infra-red region e.g. carbonyl and nitrosyl complexes IR-spectroscopy can be a powerful tool. By comparison with the spectrum of analogous soluble complexes one can draw conclusions on the structure of the immobilized metal complexes. In a study of the potential ligand sites on a surface modified silica gel, metal carbonyls were used as IR-probes to identify these sites (paper I).

One other commonly used characterization technique is ESCA, which can be used to quantitatively establish metal to ligand ratios, or to determine oxidation states of the metal on the surface. The last mentioned application has been used in many cases to prove the existence of a metallic phase [4].

A potentially important method, which has so far been applied to only few systems is solid-state NMR. This method can be used in the characterization of immobilized ligands as well as metal complexes. The usefulness of this technique has been demonstrated by Fyfe et.al. in examinations of polymer bound Pt(II) phosphine complexes [5].

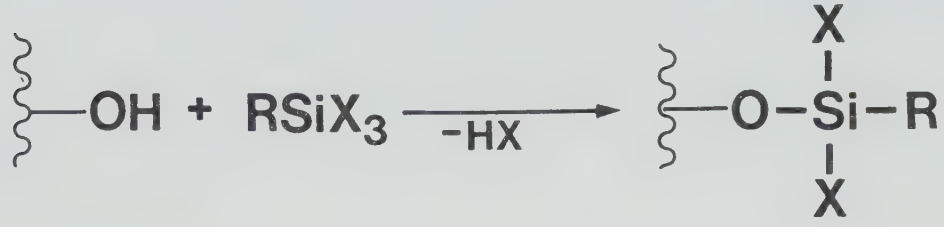
B 4. Synthesis of silica-bound ligands

The use of silica gel as support has many advantages to the more frequently used organic polymers. Silica has a more rigid structure which makes it possible to prepare a ligand system with well defined spacing of ligands. Organic polymers, on the other hand, have an inherent flexibility which can cause undesired reactions [6]. In addition, the thermal stability of silica enables the catalysts immobilized on silica to be used at higer temperatures.

The first step in the synthesis of silica-bound coordination compounds is the introduction of the metal-binding groups on the surface. This can be done by using the silanol groups on the surface. Several methods by which organic groups can be bound to silica have been described in the literature [7]. Since the bond between the metal-binding group and silica, as

pointed out above, must be stable over a wide range of reaction conditions only few of the reported methods are, however, applicable for catalytic purposes. The most important technique involves a condensation reaction between silica and organosilicon compounds viz. $R_nSi\ X_{4-n}$(n=1-3, X=Cl, OR)(eq 3).

Eq.3



This technique is a well-known one to reduce the polarity of silica for chromatographic purposes. The bonds between the organic groups and silica, viz. Si-O-Si-C have relative high thermal and hydrolytic stabilities [6]. The main difficulty in the functionalization of silica is therefore to synthesize a R_nSiX_{4-n} compund containing the desired ligating groups.

A particular great interest, judging from literature reports, has been directed to the synthesis of phosphin substituted trialkoxy silanes. The interest in phosphine chemistry orginates from the role of phosphine ligands in homogeneous catalysis. This, in turn, comes from their ability to stabilize low valent metal complexes.
The reactions most frequently used for the synthesis of silyl phosphines are hydrosilation of alkenylphosphines or photochemical additions of $HPPh_2$ to vinylsilanes [8,9]. It is important to work under anhydrous conditions when the silane is condensed on the silica surface in order to prevent polymerization of the silane. Otherwise small polymerparticles could be formed with high concentration of phosphine groups but bonded to the silica via relatively few bonds. A poorly defined ligand system with limited stability would be obtained in this way.

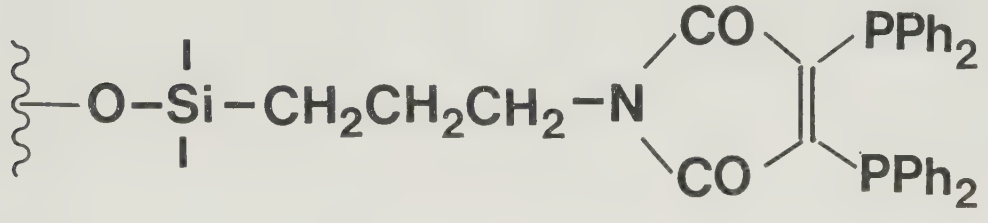
Monodentate silica-bound phosphines have been used for immobilization of metal complexes as well as of metal clusters and tested for catalytic activity [3,10]. Bartholin et.al. reported

that a Wilkinson-complex, prepared from phosphinated silica and $Rh_2Cl_2(CO)_4$, was active as catalyst for the hydrogenation of 1-hexene [11]. However, the catalytic activity was mainly caused by the presence of rhodium metal particles formed via reduction of Rh(I). The formation of a metallic phase is generally a serious problem when supported rhodium complexes are used under reducing conditions. The reduction can in many cases be observed as a drastic change of the colour of the polymer. In certain cases it has been possible to prove the presence of metal particles by electron microscopy [11] and ESCA [4,12]. It is generally believed [13] that coordinatively unsaturated species are created during the reaction which are easily reduced to give metal particles. It is, however, also possible that easily reduced metal complexes are formed already in the preparation step as discussed recently by Andersson [14].

B 5. Synthesis of silica-bound chelating ligands

One possibility to increase the stability against reduction and leakage is to use chelating bidentate ligands. Up to now rather few silica-bound chelating ligand systems have been reported in the literature. One such system, a bisphosphine, was introduced by Neuberg [15]. This ligand was prepared by reacting aminated silica with bis(diphenylphosphino) maleicacidanhydride (eq 4).

Eq.4

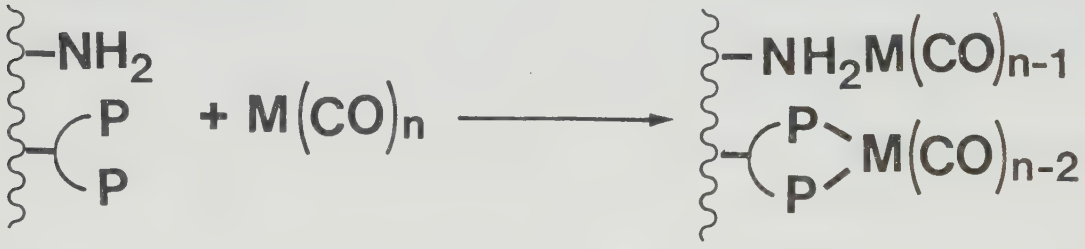


This ligand is highly attractive since a five-membered ring is formed upon metal coordination. This gives a strong chelating effect as shown by Fenske [16].

In an attempt to repeat the above described method we found that a large amount of the amine groups were left unreacted on the silica surface (Paper I).

This unreactivity of the amine groups are mainly due to hydrogen-bonding between the amine and the hydroxyl groups on the surface [17]. The amine groups can, however, be reactiv under other reaction-conditions as e.g. metal coordination resulting in the formation of a mixture of different metal complexes with varying properties. In order to study this problem metalcarbonyls were immobilized to the functionalized support. The choice of this type of metal complexes was motivated, as mentioned in chapter B3, by the ease with which carbonyl complexes can be studied by IR-spectroscopy. Since the carbonyl vibrations are sensitive to both electronic and structural changes [18], IR-spectroscopy gives a possibility to identify the formation of amine as well as bisphosphine complexes (eq 5).

Eq.5



This study showed clearly the presence of two different metal-binding groups. Obviously, those amine groups which are not reacted in the fixation of the ligands to the surface can participate in metal coordination. Since the main goal is to make well-defined ligand systems on the surface the above discussed method of synthesis must be modified. In order to obtain bisphosphines as the sole ligating specie on the surface an improved method of preparation described in paper I was developed. The condensation between the anhydride and the amine was performed in solution and the thus formed maleimide was linked without prior isolation to the silica surface. Upon reaction of the silica, funtionalized in this way, with metalcarbonyls only bisphosphine complexes were found on the silica gel. The result from this IR-investigation together with an elementary analysis of the P:N ratio show that no amine groups are left unreacted on the surface. From this study and other investigations [19] it can be concluded that methods which involve reaction between soluble and immobilized reactants often gives a mixture of products.

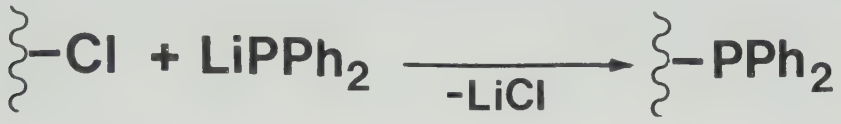
B 6. Synthesis of ligands bound to organic polymers

Phosphinated polymers can be obtained by essentially two methods.

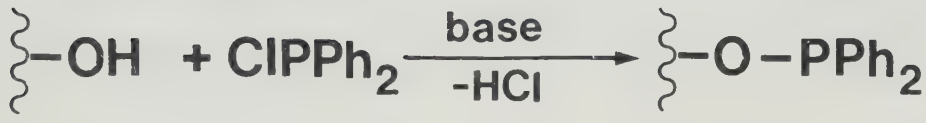
A. Polymerisation of a monomer containing a phosphine substituent.
B. Phosphination of polymeric materials.

The latter method is most commonly used since a great number of polymers which are possible to functionalize are commercialy available. A phosphine group can easily be introduced if reactive halide or hydroxyl groups are present on the polymer (eq 6-7) [20].

Eq.6



Eq.7



These synthetic methods suffer from the same type of difficulties as discussed in chapter B5. In paper III it is demonstrated that phosphination of the polymer Spheron, a copolymer of hydroxyethyldimethacrylate and ethylendimethacrylate, according to the method in eq. 7 results in only 23% conversion of the total amount of hydroxyl groups. The high degree of cross-linking of the polymer which leads to diminished accessibility of the hydroxyl groups can in part explain the low conversion. In addition hydrogen bonds between surface hydroxyl groups can further reduce their reactivity. As pointed out before, however, these groups can be reactive under other reaction conditions.

B 7. Fixation of metal complexes

A number of methods have been described by which metal complexes can be linked to functionalized supports [21]. The most important one is based upon the ligandsubstitution reaction given in eq. 8.

Eq.8 $$ML_n + L'\!\!\sim\!\!\sim \rightleftharpoons ML_{n-1}L'\!\!\sim\!\!\sim + L$$

The position of the equilibrium depends on the metal-binding ability of the exchanging ligand compared to the polymer-bound ligand. By using an exchanging ligand which is only weakly coordinated to the metal centre the equilibrium can be displaced to the right [14]. In many cases it is possible to substitute more than one ligand from the metal complex. The degree of substitution depends on the amount and distribution of the ligands on the surface. The ligands are, however, most likely not evenly distributed over the surface. A mixture of complexes with various degree of substitution will usually be obtained.

The ligand-substitution method is exemplified in paper I i.e. the preparation of immobilized metal carbonyls and in paper III i.e. the preparation of Spheron-bound molybdenum nitrosyls. In both of these papers the choice of the reacting metal complex is discussed on the basis of potential metal-binding groups on the support.

The reaction of phosphinated Spheron with either $Mo(NO)_2(pyridine)_2Cl_2$ or $Mo(NO)_2(benzonitrile)_2Cl_2$ resulted in a green polymer characterized by ν_{NO} = 1787 cm^{-1}, 1668 cm^{-1} corresponding to a bisphosphine complex. The formation of small amounts of alcolate complexes could, however, not be excluded since it was shown that $Mo(NO)_2(benzonitrile)_2Cl_2$ could be immobilized also on a non-phosphinated Spheron polymer with hydroxyls as

the only metal-binding groups. The pyridine complex, on the other hand, did not react in these circumstances.

Another important route to immobilized metal complexes is via bridge-cleavage reactions [21,22]. One example is given in paper III, viz., the reaction between the chloro bridged complex $[Mo(NO)_2Cl_2]_n$ and phosphinated Spheron. IR-studies showed clearly that a bridge-cleavage reaction took place under the formation of a $Mo(NO)_2L_2Cl_2$ complex. It must be pointed out, however, that two ligands must be present in close vicinity in order for a mononuclear $Mo(NO)_2L_2Cl_2$ complex to be formed. A nonuniform distribution of phosphine on the surface could therefore result in the binding of polynuclear species. Their remaining ligand bridges can split under catalytic conditions. Thereby metal-leaching can take place.

B 8. Immobilization of metal complexes on ion-exchangers

As pointed out in the introductory paragraph ion-exchangers can be used to immobilize charged metal complexes. This area has, however, not received the same attention as covalent attachment despite the great number of commercially available ionexchangers. The first report on this topic was published in 1969 by Haag and Whitehurst [23]. They reported that an active catalyst for the carbonylation of allylhalides could be prepared by immobilization of $Pt(NH_3)_4^{2+}$ on sulfonated polystyrene.

One problem often observed when an ionic metal complex is attached to a polymer with electrostatic forces is the leakage of metal. The degree of metal-leakage can however be controlled by variation of the ratio between the amount of ion-exchanger and the solvent volume as shown by Drago [24].

Another complication with ion-exchangers having carboxylate and sulfonate groups are that these groups, in addition to their role as counter-ions, have a complex-binding ability. This can seriously affect the catalytic properties of the immobilized metal complexes.

An attempt was made to use the cationic rhodium complex viz. Rh(norbornadien)L_2^+ (L_2=bisdiphenylphosphinoethane), attached to sulfonated polystyren, as hydrogenation catalyst. Only a very low activity was observed (Paper II). The analogous homogeneous complex with paratoluenesulfonate as counter-ion was, however, very active, while the addition of an excess of paratoluene-sulfonic acid to this system totally inhibited its catalytic activity. The complex-binding of the sulfonate ligand to the active species would result in the formation of a coordinatively saturated species with no catalytic properties. It is therefore probable that the polymer-bound sulfonate groups act in the same manner.

C. OLEFIN METATHESIS

C 1. Introduction

Olefin metathesis can be defined as a catalytic cleavage and reformation of carbon-carbon double bonds (eq 9).

Eq.9

$$\begin{matrix} CH_2=CH-CH_3 \\ + \\ CH_2=CH-CH_3 \end{matrix} \rightleftharpoons \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + \begin{matrix} CH-CH_3 \\ \| \\ CH-CH_3 \end{matrix}$$

The reaction is essentially thermoneutral ($\Delta H \approx 0$) for acyclic olefins resulting in an equilibrium mixture of products corresponding to a statistical distribution of alkyliden groups (=C).

The first report on this remarkable reaction was published in 1964 by Banks and Bailey [25]. They showed that linear olefins can be disproportionated over hetereogeneous catalysts prepared from molybdenum or tungstenhexacarbonyls adsorbed on aluminium oxide. This discovery was soon utilized in a commercial process for the preparation of high-purity ethylen from propylen, i.e. the Phillips triolefin process [26]. Three years later (1967) the first system of homogeneously catalyzed metathesis was introduced by Calderon and co-workers [27]. They found that WCl_6 in the presence of an equimolar amount of ethanol could be activated for metathesis of 2-pentene by the addition of ethylaluminiumdichloride ($EtAlCl_2$). This system is characterized by a very high activity and selectivity. E.g., 10^4 mole of 2-pentene per mole WCl_6 can be converted to an equilibrium mixture in a few seconds.

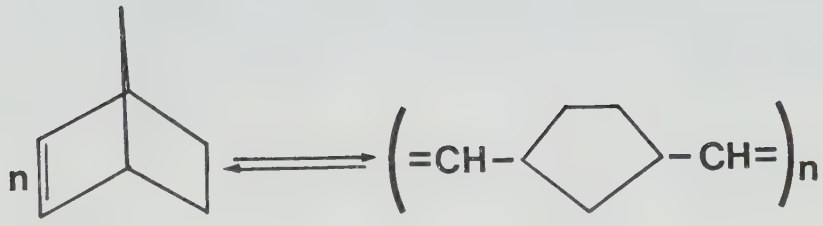
Reaction types

Three different reaction types can be recognized depending on the type of the olefin substrate viz. selfmetathesis (eq 9), cross-metathesis (eq 10) and ring-opening polymerisation (eq 11).

Eq.10

$$CH_3CH=CHCH_2CH_3 + CH_2=CH_2 \rightleftharpoons CH_3CH=CH_2 + CH_2=CH-CH_2CH_3$$

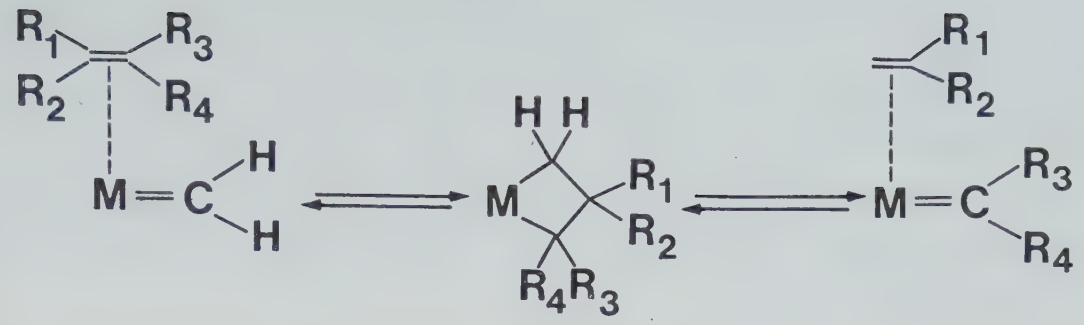
Eq.11



Because of the great possibility of variation olefin metathesis can be used as a general method in the synthesis of polymeric as well as simple olefins. Application of the ring-opening polymerisation reaction has resulted in a number of new and potential technically useful polymers. For instance a polymer with biocidic activity has been prepared by ring-opening polymerisation of 11-tributylstannyl-tricyclo-tridec-5-ene [28]. Olefin metathesis can also be applied to olefins with more than one double bond. Because of the great variety of products formed via inter and intramolecular metathes [29] this application is, however, of limited synthetic value.

C 2. The carbene mechanism

The first general reaction scheme for the olefin metathesis was presented by Bradshaw in 1967 [30]. This mechanism involved a pairwise exchange of alkylidene fragments between two olefins coordinated to the catalytic centre. The Bradshaw-mechanism can not, however, satisfactorily explain the composition of the product mixtures [31]. For that reason another mechanism was proposed, which did not involve a pairwise exchange of olefins. In this mechanism the formation of metalcarbenes and metallacyclobutanes as intermediates is the crucial point (eq 12).



Eq.12

Until a few years ago only indirect evidences, such as product patterns, in favour of this mechanism had been found. The proposed intermediates had not been detected or isolated. The development of new methods for the preparation of metal carbenes and metallacyclobutanes have, however, created the necessary conditions for detailed studies. Kress and Osborn [32] showed that 2-pentene underwent metathesis in presence of the carbene complex $Me_3CCH{=}WBr_2(OCH_2CMe_3)_2$ and $AlBr_3$. By the use of NMR-spectroscopy the two possible propagating carbenes, viz. $W{=}CHCH_3$ and $W{=}CHCH_2CH_3$ was identified. Schrock and co-workes have also shown that metal carbenes are intermediates in the olefin metathesis reaction [33]. The existence of a metallacyclobutane intermediate is more doubtful. It has been observed, however, that cyclopropanes are often formed as by-products in the olefin metathesis reaction [62]. From studies on stable platinacyclobutanes it is well-known that thermal decomposition gives cyclopropanes as a result of a reductiv elimination. Grubbs has shown that cyclopentadienyltitaniumcyclobutanes can be prepared from carbenes. They exchange olefins with the formation of a new metallacyclobutane [34]. Another observation which supports the existence of a metallacyclobutane intermediate is the (E/Z)-stereoselectivity data reported by Basset et.al. [35].

C 3. Catalyst systems

A great number of catalyst systems for olefin metathesis have been described in the literature [36]. Some selected systems are shown in table 1.

Table 1.

Catalyst system	Reference
$WCl_6/LiAlH_4$	[37]
$WCl_6/SnMe_4$	[29]
$Mo(NO)_2(PPh_3)_2Cl_2/EtAlCl_2$	[38]
$Re(CO)_5Cl/EtAlCl_2$	[39]
$Mo(CO)_6/Al_2O_3$	[25]
$Re_2O_7/SnMe_4/Al_2O_3$	[40]

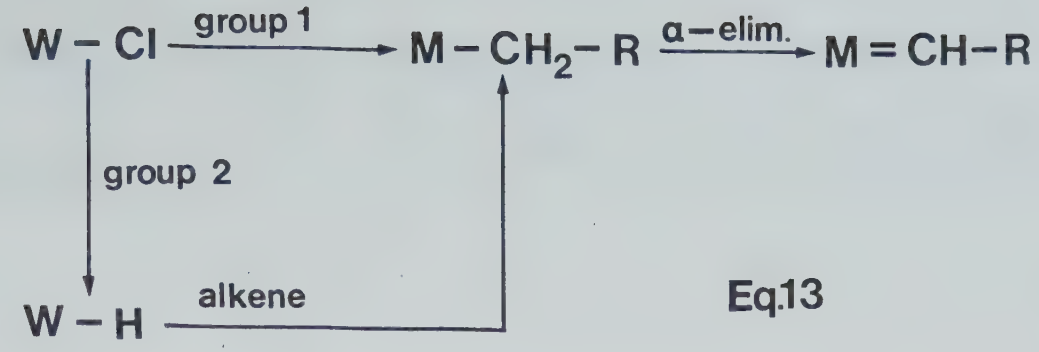
Most of the catalyst systems are based on the transition elements molybdenum, tungsten or rhenium. Exceedingly few systems based on other elements have been described. Besides the transition metal compound a cocatalyst e.g. $EtAlCl_2$ or $SnMe_4$ must be added to make an active catalyst.

In the following discussion only homogeneous catalyst systems will be taken into account. Several catalyst systems with high activity and selectivity can be found in this group.

C 3:1. WCl_6-based systems

The most well-studied homogeneous catalyst system is WCl_6 associated with a cocatalyst [36]. The presence of the latter is essential to obtain activity. The cocatalyst can be divided into two groups 1) alkylating agents e.g. $EtAlCl_2$ 2) Hydride donors e.g. $LiAlH_4$, $HSiMe_3$. The action of these reagents on WCl_6 creates the necessary conditions for the formation of an initial carbene.

By the direct alkylation with a "group 1" reagent a metal-alkyl is formed (eq 13). This can by α-elimination form the carbene. Alternatively, by the reaction of a "group 2" reagent a hydride-complex can be formed. This complex can form the carbene via the insertion of an alkene in the metal-hydride bond (eq 13).



Eq.13

By the use of deutarated cocatalyst it has been possible to prove [42,43] that the initial carbene is formed as a result of such reactions. The effectivity of the carbene generating step has been determined by examination of the products formed during the first catalytic cycle. For the system $WCl_6/SnMe_4$ Grubbs and Hoppin showed that only 8% of the total amount of WCl_6 was converted to propagating carbenes [43]. This low yield might be due to competing reactions such as carbene dimerization and reductive elimination [42]. Since the most active systems are obtained if the cocatalyst has Lewis-acidic properties its role can not only be restricted to its alkylating ability [36,41]. How the presence of a Lewis affects activity is discussed in the following section.

C 3:2. The catalyst system WCl_6/allyltrimethylsilane

In paper IV and V it is demonstrated that allyltrimethylsilane (ATMS) is able to activate WCl_6 for the metathesis of acyclic olefins. The activating power of this alkenylsilane depends on its allylating properties towards WCl_6. By such an allyl-transfer the conditions necessary for the formation of an initial carbene is fullfilled, as discussed above. The reaction between WCl_6 and ATMS is accompanied by the formation of chlorotrimethylsilane which is related to the transfer of a chlorine atom from tungsten to silicon. The reactivity of allyltrimethylsilane towards electrophilic reagents is well-known [57, 64] (eq 14).

Eq.14

The cleavage of silicon-allyl bonds with coordination compounds of palladium and mercury has been observed [71]. In both these cases stable metal-allyl compounds are formed.

The induction period

In the cross-metathesis of allyltrimethylsilane with Z-2-penten in the presence of WCl_6 an induction period of about 5 minutes was always observed. If ATMS was added 5 minutes before the addition of Z-2-pentene, however, an immediate formation of products was observed. The induction period can thus be related to the reaction between WCl_6 and ATMS. On addition of a Lewis acid viz. $AlBr_3$ or $AlCl_3$, Al/W=0.2-2 no induction period was observed. This means that AlX_3 plays an active role in the initiation step. Two possible explanations is put forward in paper V. a) AlX_3 acts as a catalyst for the transfer of allyl-groups from silicon to tungsten via the formation of an intermediate allylaluminiumhalide. This property of AlX_3 has been studied by Bordeau et.al. [65] in the methylation of $GeCl_4$ with $SiMe_4$. b) AlX_3 acts by abstracting a chlorine ligand from WCl_6 and thus increasing the electrophilic character of tungsten. This would facilitate the coordination of ATMS as well as cleavage of the allyl-silicon bond. The addition of a Lewis base instead of AlX_3 should diminish the possibility for WCl_6 to form an olefin complex with ATMS. This was indeed observed as an increase of the induction period when diethylether was added.

Activity

The activity was also greatly affected by the addition of AlX_3. The initial activities was considerably increased as shown in fig 1, paper V. The maximum initial rate was obtained at a Al/W ratio of 0.4 and was found to be essentially the same at higher ratios. Considering the overall activity, however, a fast deactivation occured at higher Al/W ratios ($\geq$ 1).

In addition, the (E/Z)-stereoselectivity is also greatly affected by the addition of aluminiumhalide. Since the (E/Z)-stereoselectivity is determined by the steric and electronic nature of the propagating species [35,36] the reported data indicates that AlX_3 plays an active role in the propagating step [45,46]. It can thus be concluded that presence of a Lewis acid affects initiation, propagation as well as the termination steps.

C 3:3. Catalyst systems based on molybdenum nitrosyl complexes

The complex $Mo(NO)_2L_2Cl_2$ (L=pyridine, PR_3) associated with organoaluminium compounds such as $EtAlCl_2$ and $Et_3Al_2Cl_3$ is a very active catalyst for metathesis of terminal as well as internal olefins [49]. This is one of the few systems which exhibits a ligand effect on the activity (pyridine>PPh_3>$AsPh_3$) [47]. This implies that the ligands are still bound to the metal centre during the propagating step [47]. Consequently this system is suitable to heterogenize on a solid support using the ligands (L) as links. One such example is described in paper III and summarized in chapter C4.
Besides its high activity the system $Mo(NO)_2L_2Cl_2/EtAlCl_2$ is characterized by a high (E/Z)-stereoselectivity compared to other systems [35].

C 3:4. Reaction conditions

The homogeneous catalyst systems are active under mild conditions, i.e. atmospheric pressure and low temperature 0-75°C. The reactions must be done under rigorous exclusion of oxygen and water i.e. high purity inert-gas (N_2,Ar) and oxygen-free, well dried solvents must be used. As reaction media for the above mentioned catalyst systems chlorobenzene is normally used because of its solvating power and its resistance to alkylation. Indeed the latter effect turns out to be a serious problem when toluen is used as solvent for the catalyst system $WCl_6/EtAlCl_2$ [50].

C 4. Polymer-bound metathesis catalyst systems

Two principal different methods to prepare a polymer-bound catalyst system for the olefin metathesis reaction have been published [48,66-69]. These are:

1. Reaction between a polymer-bound cocatalyst and a transition metal complex.

2. Immobilization of a transition metal complex to a functionalized support, followed by addition of cocatalyst.

The first mentioned method has been used to immobilize WCl_6 based systems [69,70]. The synthesis of two different polymer-bound cocatalysts have recently been described in the literature (-$SnMe_3$, - AlEtCl) [69,70]. Reaction between these immobilized cocatalysts and WCl_6 gives a heterogeneous system which is activated at the same time as tungsten is bonded to the polymer. The activity is, however, rather low compared to that of analogous homogeneous systems. From a mechanistic point of view the reported results e.g. metal-leaching studies are interesting since they indicate that a stable bond is established between the cocatalyst and the transition metal complex.

Method 2 is restricted to metal complexes bearing ligands which can be easily linked to a support. From experimental investigations [41] it is well-known that phosphine or pyridine substituted tungsten or molybdenum carbonyls ($M(CO)_{6-x}L_x$) in presence of aluminiumalkyls are active as metathesis catalysts. Moreover, by using the pyridine or phosphine ligand belonging to these complexes, they can be prepared in a heterogeneous form with the ligand bound to the support. Such polymer-bound complexes have also attained a considerable interest [66-68] and such systems together with alkylaluminiumhalides have been shown to give a moderate activity for metathesis of internal olefins [66-68]. A more active system can be prepared from polymer-bound molybdenum nitrosyl complexes viz. $Mo(NO)_2L_2Cl_2$ [48, III]. The method of synthesis of such polymer-bound complexes have been described in chapter B7.

Olefin metathesis by polymer-bound molybdenum nitrosyl complexes

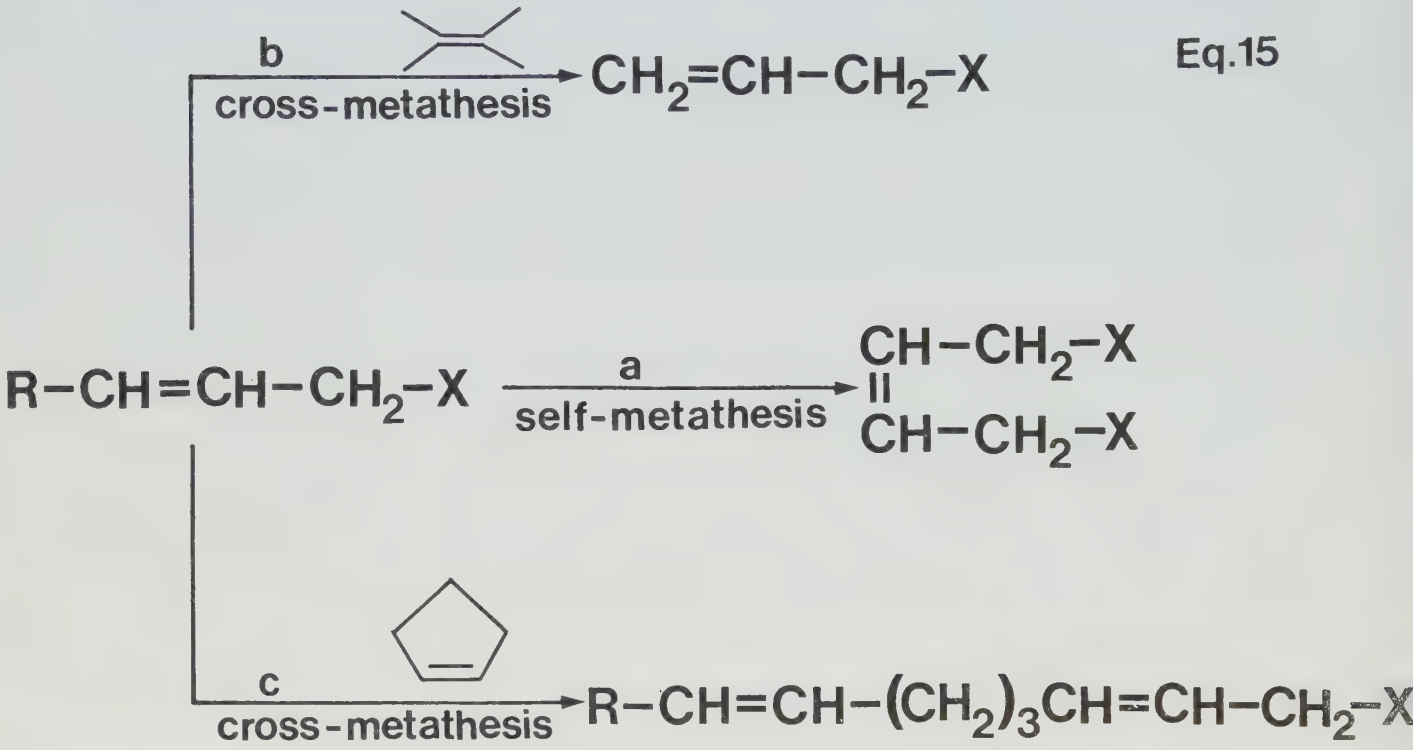
$Mo(NO)_2L_2Cl_2$ immobilized on the polar polymer Spheron can be activated by treatment with $EtAlCl_2$. For the analogous homogeneous system a ratio of $EtAlCl_2/Mo=6$ is required to give maximum activity [49]. For the polymer-bound system a much higher ratio of cocatalyst to molybdenum was needed to reach the highest activity. Maximum activity was found at about 7 mmol $EtAlCl_2$ per gram of polymer, in most cases corresponding to Al/Mo about 50. This high ratio indicates an extra need for the cocatalyst. This is mainly caused by reactions between the cocatalyst and the polar groups on the polymer. Two such reactions were observed a) Hydrolysis of $EtAlCl_2$ by reaction with hydroxylgroups on the polymer; b) Formation of complexes between $EtAlCl_2$ and carbonyl groups. These reactions take a high toll on the available amount of $EtAlCl_2$. Therefore only a low proportion of active molybdenum complexes are formed at low concentrations of cocatalyst, resulting in a low actvity. Neutralisation of the Lewis basic sites can, however, have a positive effect since these groups are known to act as catalyst inhibitors in metathesis. This will be discussed further in chapter C5.

The activity of the polymer-bound systems at optimum conditions was comparable to that of the analogous homogeneous system $Mo(NO)_2(PPh_2OBu_4)_2Cl_2/EtAlCl_2$.
It is also interesting to compare the (E/Z)-stereoselectivity data of homogeneous and of the heterogenized systems. In this respect the polymerbound system (E/Z=0.22-0.26) is very similar to homogeneous systems (E/Z=0.20-0.24). Thus the immobilization procedure has not changed the catalytic behaviour of the system.

C 5. Metathesis of functionalized olefins

Application of the olefin metathesis reaction to alkenes bearing a functional group is a attractive route to the synthesis of a great number of valuable mono and difunctionalized olefins. Disubstituted olefins can be obtained via selfmetathesis of substituted acyclic olefins (eq 15a).

Cross-metathesis of functionalized acyclic olefins with acyclic olefins (eq 15b) or cyclic olefins (eq 15c) can give shorter or longer homologous, respectively. As pointed out before the number of combinations is very large.



Eq.15

Most of the functional groups that contain a heteroatom have however a negative influence on the metathesis activity. Several reasons for this inhibiting effect have been suggested, e.g., by Grubbs [31]. Destruction of the active centre by irreversible reactions of Wittig type has been observed for ketones, aldehydes and esters. When the substrate is an ester, nitrile or ether, the complexation between these groups of Lewis base character and the catalytic centre renders the coordination of an olefin more difficult. A decrease in the Lewis basicity would shift the position of the equilibrium and result in an increase of the activity. Also adding a Lewis acid which coordinates strongly to the Lewis base will shift the equilibrium. This is illustrated in paper III were the activity of the system $Mo(NO)_2(PPh_3)_2Cl_2/nEtAlCl_2$ was studied in the metathesis of Z-2-pentene in the presence of an excess of methylstearate (ester/Mo=39). Addition of 6 equalents of $EtAlCl_2$ per mole Mo resulted in a totally inactive system. The activity

could however be increased by the addition of larger amount of cocatalyst ($EtAlCl_2$/Ester $\geq$ 1). Complexation between the cocatalyst and the ester reduces the possibility of the latter to block the catalytic centre. The complex formation was followed using infra-red spectroscopy. From these measurements and the activity measurements it can be concluded that the activity is low for conditions when the complex formation is low i.e. there are large quantities of free ester that can poison the catalytic system [III]. The possibility to block Lewis basic groups in a reversible way has also been used by Streck [28] in the ring-opening polymerisation of cyclopentene in presence of esters and nitriles and by Edwidge et.al. in the metathesis of amines [54.55].

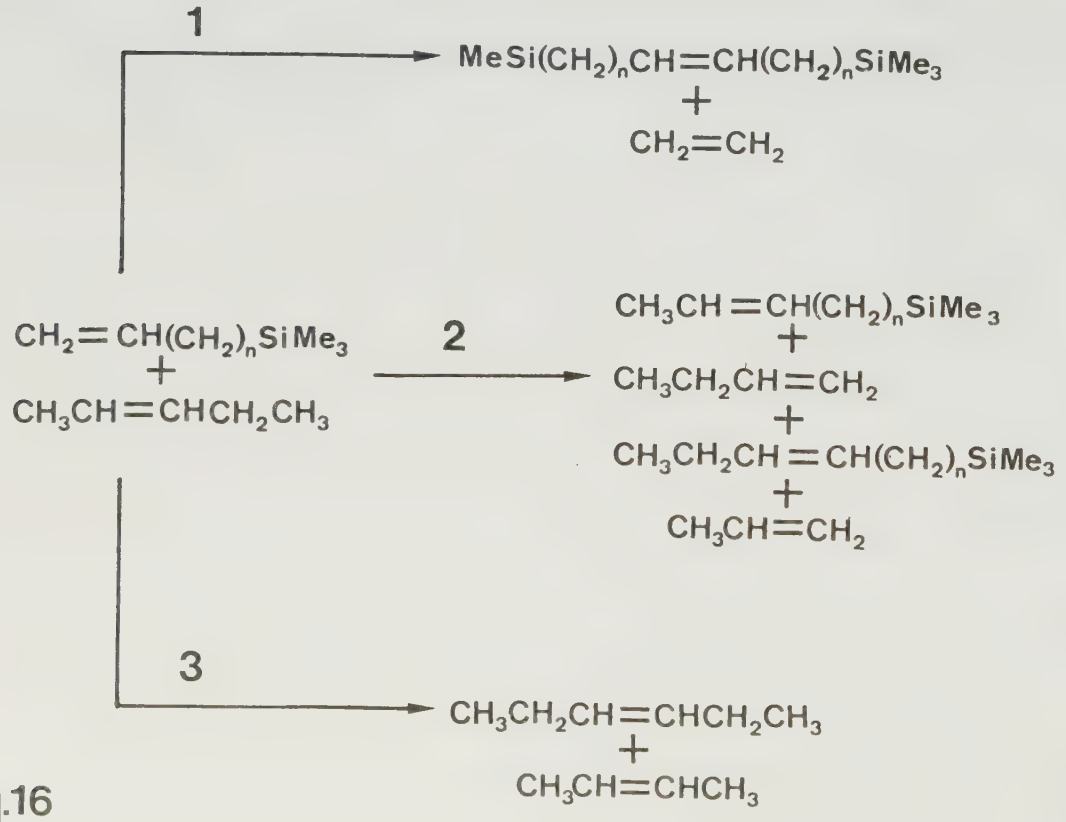
Except for the system $Mo(NO)_2L_2Cl_2/EtAlCl_2$ relatively few systems have proven themselves active for the metathesis of functionalized olefins. The most well-known system in this category is $WCl_6/SnMe_4$ originally introduced by van Dam et.al. [51]. These authors found that methyloleate was converted to 9-octadecen and dimenthyl-9-octadecenedioate in presence of this system. The system can also be applied to the metathesis of other substituted olefins such as ethers [52], nitriles [53] and alkenylsilanes [IV,V]. A generalization from these studies is that the double bond and the functional group in the olefin must be separated by at least one methylene group ($-CH_2-$) in order to obtain metathetical conversion. The failure of such substances to undergo selfmetathesis can be due to a strong propensity for degenerate metathesis, enhanced by the greater polarity of the double bonds [42].

C 6. Metathesis of alkenylsilanes

In comparison with other functionalized olefins e.g. esters and nitriles few reports have emerged concerning metathesis of alkenylsilanes. However, alkenylsilanes have become increasingly important as synthetic intermediates in organic chemistry [57.58]. Therefore the development of new and powerful methods for the synthesis of this class of compounds is well-motivated. In this development olefin metathesis can be an important tool.

Another useful application of organosilanes has been demonstrated by Streck [28]. By olefin metathesis alkenyltrichlorosilanes can be incorporated in polyalkenamers.

Some few catalysts for metathesis of alkenylsilance have been reported viz. MoO_3/Al_2O_3 [59], Re_2O_7/Al_2O_3 [60]. In paper IV and V it is shown that also homogeneous systems based on WCl_6 work well for the metathesis of silyl olefins. The systems were principally tested under cross-metathetical conditions. Specifically, the alkenylsilane $CH_2=CH(CH_2)_nSiMe_3$ (n=0,1,2) and Z-2-pentene were reacting together. Under these conditions three different reactions can occur as exemplified in equation 16. (1) selfmetathesis of the alkenylsilane (eq 16.1). (2) cross-metathesis (eq 16.2). (3) Selfmetathesis of Z-2-pentene (eq 16.3). If an alkenylsilane is inactive in reactions (1) and (2) its eventual inhibiting effect can be studied via reaction (3).



Eq.16

This means that metathesis under such conditions is a sensitive indicator of how the functional group influences the activity [58].

In the application of the system $WCl_6/SnMe_4$ to the cross-metathesis of vinyltrimethylsilane (VTMS) and Z-2-pentene no reactions (eq 16.1-16.3) at all were observed. That even reaction 16.3 is blocked indicates that VTMS plays the role of a catalyst inhibitor. This poisoning effect is pronounced even at very low VTMS/W ratios e.g. 2 equivalents of VTMS per mole of WCl_6 totally inhibited the metathesis of Z-2-pentene with the system $WCl_6/SnMe_4$ [IV]. A similar strong inhibiting effect by VTMS has also been observed by Dolgoplosk et.al. [56] in the ring-opening polymerisation of cyclopentene with the system $(RO)_2\ WCl_4/EtAlCl_2$ ($R=CH(CH_2Cl)_2$). Allyltrimethylsilane and 3-butenyltrimethylsilane, on the other hand, were readily converted to cross-products in the presence of the system $WCl_6/SnMe_4$ [IV]. This points to the importance of the spacing between the double bond and the functional group (vide infra). It can therefore be concluded that one methylen group must be present between the double bond and the trimethylsilyl group in order to obtain activity. The reason for the inhibiting power of VTMS has been discussed by Dolgoplosk [61]. He proposed that a stable non-propagating carbene i.e. $W=CH-SiMe_3$ is formed.

Besides the above discussed system $WCl_6/SnMe_4$ also other WCl_6-based systems were found to applicable to metathesis of alkenylsilanes. Allyltrimethylsilane was for instance found to be effectively metathetically converted to cross-products by WCl_6 without any addition of cocatalyst. In this system ATMS plays a dual role in acting both as catalyst initiator and as a substrate (vide infra). The activity of this system can be markedly increased by the addition of small amount Lewis acids viz. AlX_3 (X=Cl,Br) [V]. This system is in fact the most active system found for metathesis of allyltrimethylsilanes. On the other hand 3-butenyltrimethylsilane was only able to activate WCl_6 to a very low degree as noted by the very low activity in the cross-metathesis of 3-butenyltrimethylsilane and Z-2-pentene. As was observed for ATMS addition of $AlBr_3$ changes the system substancially creating a highly active system.

One disadvantage of the above reported WCl_6 based system are their low activity in selfmetathesis of alkenylsilanes (paper IV). This is, however, not surprising since it is well-known

that tungsten based catalyst systems normally gives low product yields in the metathesis of terminal olefins [42]. The reason for this is that instead of productiv metathesis, forming new olefins, a non-productiv reaction route dominates [62]. Katz et.al. determined the ratio between the productiv and the non-productive metathesis of 1-heptene to a value of 80-160 for WCl_6 based systems [63]. This shows the preference for a degenerative reaction route in the metathesis of terminal olefins. Therefore, in order to prepare alkenyldisilanes via olefin meathesis other catalyst systems must be applied.

D. ACKNOWLEDGEMENTS

I wish to express my sincere gratitude to Dr. Carlaxel Andersson and Prof. Ragnar Larsson for introducing me to the field of catalysis and for their inspiring interest and genereous support of this work.

I am grateful to Prof. Sten Ahrland who has put every facility at my disposal.

I also wish to thank the following:

Mrs Sylvia Flato for her skilful assistance in experimental work and for having drawn the figures.

Dr Börje Folkesson for valuable help in the measurement and interpretation of ESCA-spectra.

Dr Berndt Rebenstorf for introducing me into vaccum and inert-gas technique and for inspiring discussions.

Ms Carina Folkesson for typing this manuscript.

Mr Ove Hansson for skilful technical assistance.

My wife Maria for her patience and encouragement during this work.

Finally, I wish to extend my gratitudes to my colleagues for enjoyable collaboration and stimulating discussions.

Financial supports from Styrelsen för Teknisk utveckling (Swedish Board of Technical Development), the Royal Physiographic society, the Royal Swedish Academy of Sciences and AB Karlshamns oljefabriker are gratefully acknowledged.

E. REFERENCES

[1] J.F. Young, J.A. Osborn, F.H. Jardine and G. Wilkinson
Chem. Commun. (1965) 131

[2] J.P. Collman and L.S. Hegedus
Principles and applications of Organotransition. Metal Chemistry, Univ. Science Books (1980)

[3] M.S. Scurell
Catalysis, Chem. Soc., 2(1978) 215

[4] C. Andersson and R. Larsson
J. Catal., 81(1983) 194

[5] C.A. Fyfe, H.C. Clark, J.A. Davies, P.J. Hayes and R.E. Wasylishen
J. Am. Chem. Soc., 105(1985) 6577

[6] D.C. Bailey and S.U. Langer
Chem. Rev., 81(1981) 109

[7] K.K. Unger
Porous silica, Elseiver, New York (1979)

[8] K.G. Allum, R.D. Hancock, I.W. Howell, S. McKinzie, R.C. Pitkethly and P.J. Robinson
J. Org. Metal Chem., 87(1975) 203

[9] S.I. Woo and C.G. Hill
J. Mol. Catal., 15(1982) 309

[10] K.G. Allum, R.D. Hancock, I.W. Howell, T.E. Lester, S. McKenzie, R.C. Pitkethly and P.J. Robinson
J. Org. Metal. Chem., 107(1976) 393

[11] M. Bartholin, C. Graillat, A. Guyot, G. Coudurier, J. Bandiera and G. Naccache
J. Mol. Catal., 3(1977/78) 17

[12] A. Luchetti, L.F. Wieserman and D.M. Hercules
J. Phys. Chem., 85(1981) 549

[13] A. Guyot, C. Graillat and M. Bartholin
J. Mol. Catal., 3(1977/78) 39

[14] C. Andersson and R. Larsson
J. Catal., 81(1983) 179

[15] K.M. Neuberg
PhD Thesis, Stanford University (USA) 1979

[16] D. Fenske and H.J. Becher
Chem. Ber. 107(1974)117

[17] S.I. Woo and C.G. Hill
J. Mol. Catal., 29(1985) 209

[18] F.A. Cotton and G. Wilkinson
Advanced Inorganic Chemistry, John Wiley 1980, Chapter 25

[19] H. Engelhardt and D. Mathes
J. Chrom., 142(1977) 311

[20] J. Lieto, D. Milstein, R.L. Albright, J.V. Minkiewicz and B.C. Gates
Chemtech (1983) 46

[21] F.R. Hartley and P.N. Vezey
Adv. Organomet. Chem., 15(1977) 189

[22] Z. Michalska
J. Mol. Catal., 19(1983) 345

[23] W.O. Haag and D.D. Whitehurst
German Patent 1, 800, 371

[24] R.S. Drago, E. Nyberg, A. ElAmma and A. Zombeck
Inorg. Chem., 20(1981) 641

[25] R.L. Banks and G.C. Bailey
Ind. Eng. Chem. Prod. Res. Dev., 3(1964) 170

[26] R.L. Banks, D.S. Banasiak, P.S. Hudson and J.R. Norell
J. Mol. Cat., 15(1982) 21

[27] N. Calderon, H.Y. Chen and K.W. Scott
Tetrahedron Lett., (1967) 3327

[28] R. Streck
J. Mol. Catal., 15(1982) 3

[29] E. Verkuijlen and C. Boelhouwer
J. Chem. Soc. Commun., (1974) 793

[30] C.P. Bradshaw, E.J. Howman and L. Turner
J. Catal., 7(1967) 269

[31] R.H. Grubbs
Comprehensiv Org. Metal. Chem., Eds G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon Press, 1982, Chapter 54

[32] J. Kress, M. Wesolek and J.A. Osborn
J. Chem. Soc. Chem. Commun., (1982) 514

[33] R. Schrock, S. Rocklage, J. Wengrovious, G. Rupprecht and J. Fellman
J. Mol. Catal., 8(1980) 73

[34] K.C. Ott, J.B. Lee and R.H. Grubbs
J. Am. Chem. Soc., 104(1982) 2942

[35] N. Taghizadeh, F. Quignard, M. Leconte, J.M. Basset, G. Larroche, J.P. Laval and A. Lattes
J. Mol. Catal., 15(1982) 219

[36] V. Dragutan, A.T. Balaban and M. Dimonie
Olefin metathesis and ring-opening polymerisation, John Witey and Son, 1985, Chapter 2

[37] S.A. Matlin and P.G. Sammes
J. Chem. Soc. Perkin 1, (1978) 624

[38] E.A. Zuech, W.B. Hughes, D.H. Kubicek and E.T. Kittleman
J. Am. Chem. Soc., 92(1970) 528

[39] M.F. Farona and W.S. Greenlee
J. Chem. Soc. Chem. Commun., (1975) 759

[40] R.H.A. Bosma, G.C.N. van den Aaardweg and J.C. Mol
J. Org. Metal. Chem., 255(1983) 159

[41] L. Ramain and Y. Trambouze
Compt. Rend. Acad. Sci. C., 273(1971) 1409

[42] K.J. Ivin
Olefin metathesis, Academic Press, London, 1983

[43] R.H. Grubbs and C.R. Hoppin
J. Chem. Soc. Chem. Commun., (1977) 634

[44] J-L. Wang, H.R. Menapace and M. Brown
J. Catal., 26(1972) 455

[45] J. Kress and J.A. Osborn
J. Am. Chem. Soc., 105(1983) 6346

[46] E.L. Muetterties
Inorg. Chem., 14(1975) 951

[47] W.B. Hughes
Adv. Chem. Ser., 132(1974) 192

[48] R.H. Grubbs, S. Swetnick and S.C-H. Su
J. Mol. Catal., 3(1977/78) 11

[49] W.B. Hughes
J. Am. Chem. Soc., 92(1970) 532

[50] J. Beger, R. Sass and G. Zimmerman
J. Prakt. Chem., 319(1977) 790

[51] P.B. van Dam, M.C. Mittelmeijer and C. Boelhouwer
J. Chem. Soc. Chem. Commun., (1972) 1221

[52] W. Ast, G. Rheinwal and R. Kerber
Recl. Trav. Chim. Pays-Bas, 96(1977) M127

[53] R.H.A. Bosma, G.C.N. van den Aaardweg and J.C. Mol
J. Org. Metal. Chem., 280(1985) 115

[54] C. Edwige, A. Lattes, J.P. Laval, R. Mutin, J.M. Basset and R. Nouguier
J. Mol. Catal., 8(1980) 297

[55] R. Nougier, R. Mutin, J.P. Laval, G. Chapelet, J. Basset and A. Lattes
Recl. Trav. Chim. Pays-Bas., 96(1977) M91

[56] I.A. Kopeva, I.A. Oreshkin, E.I. Tinyakova and B.A. Dolgoplosk
Dokl. Akad. Nauk. SSSR, 249(1979) 374

[57] T.H. Chan and I. Fleming
Synthesis (1979) 761

[58] D.A. Armitage
Comprehensive Org. Metal. Chem., Eds G. Wilkinson, F.G.A. Stone and E.W. Abel, Pergamon Press, 1982, Chapter 9

[59] R.A. Friedman, S.M. Nosakova, Y.B. Krykov, A.U. Bashirov, N.S. Nametkin and V.M. Vdovin
Izv. Akad. Nauk. SSSR, Ser. Khim., 20(1971) 2100

[60] E.S. Finkelshtein, E.B. Porthykh, N.V. Ushakov and V.M. Vdovin
Izv. Akad. Nauk. SSSR, Ser. Khim., 29(1980) 641

[61] B.A. Dolgoplosk
J. Mol. Catal., 15(1982) 193

[62] R.H. Grubbs
Progr. Inorg. Chem., 24(1978) 1

[63] J. McGinnis, T.J. Katz and S. Hurwitz
J. Am. Chem. Soc., 98(1976) 605

[64] A.W.P. Jarvie
Org. Metal. Chem. Rev.A., 6(1970) 153

[65] M. Bordeau, S.M. Djamei and J. Dunoques
Organometallics, 4(1985) 1087

[66] J.M. Basset, R. Mutin, G. Descotes and D. Sinou
C.R. Acad. Sci., Ser. C, 280(1975) 1181

[67] S. Warwel and P. Buschmeyer
Angew. Chem., 90(1978) 131

[68] S. Tamagaki, R.J. Card and D.C. Neckers
J. Am. Chem. Soc., 100(1978) 6635

[69] A. Uchida and M. Ko-ori
J. Mol. Catal., 28(1985) 209

[70] S. Swetnick
Ph.D-Thesis, Michigan State University (USA) 1979

[71] I. Haiduc and V. Popa
Adv. Org. Metal. Chem., 15(1977) 113

I

Journal of Organometallic Chemistry, 258 (1983) 195–204
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

CHELATING PHOSPHINES ON SILICA GEL

I. CARBONYL COMPLEXES AS A MEAN TO PROBE CHELATING LIGAND SITES

MATS BERGLUND, CARLAXEL ANDERSSON and RAGNAR LARSSON

Division of Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740 S-220 07 Lund (Sweden)

(Received July 26th, 1983)

Summary

Two methods for the preparation of the silica-bound chelating phosphine ligand bis(diphenylphosphino)maleimide have been studied. In the first a silica surface with bound amine groups is treated with bis(diphenylphosphino)maleic acid anhydride. By use of different Group VI carbonyl complexes $M(CO)_6$, $M(CO)_4L$ (M = Cr, Mo, W; L = norbornadiene) and $M(CO)_5Cl^-$ as IR probes it is shown that this method yields two different types of metal-binding sites on the gel, involving amine groups and bidentate phosphine groups, respectively.

In the second method bis(diphenylphosphino)maleic acid anhydride is treated with 3-aminopropyltriethoxysilane and the imide formed by this reaction is, without isolation, further condensed on the silica surface. Use of the same type of IR probes as in the first route shows that the silica gel in this case contains the bidentate phosphine group as the sole metal-binding site.

The preparations of new metal tetracarbonyl complexes for Cr, Mo and W bound to silica via bidentate phosphino groups are described.

Introduction

Chemical modification of surfaces of various supports has attracted much interest in recent years. The technique has found applications in several fields, e.g. matrix-binding of enzymes and co-factors [1], provision of stationary phases for gas and liquid chromatographic purposes [2,3], modification of electrodes [4], and the immobilization of homogeneous metal complex catalysts [5–12]. For catalytic applications two types of supports have been most frequently used, viz. polystyrene [5] and silica gel [13,14]. At present a number of synthetic procedures are known by which phosphines can be linked to polystyrene supports [5,15,16], and oxide supports can be phosphinated by the use of phosphine substituted silanes, e.g.

0022-328X/83/$03.00 © 1983 Elsevier Sequoia S.A.

$R_2P(CH_2)_nSiX_3$ (X = alkoxy, chloro). The studies have mainly involved monodentate phosphine ligands.

Recent studies on catalytic reactions by metal complexes linked to solid supports

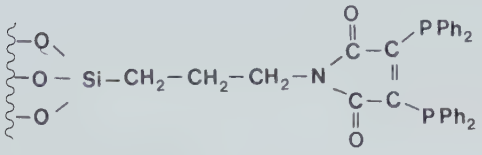


Fig. 1. The silica-bound bidentate phosphine ligand.

via monodentate phosphines have revealed that in many cases these catalysts are unstable with respect to reduction [17–19] and metal leaching [20,21]. This instability is not surprising, since in many examples of catalytic cycles involving metal complexes a metal–ligand dissociation reaction is a key step in creating a vacant coordination site. To improve catalyst stability the use of chelating ligands seems to offer a useful approach. This idea has been put forward by Marquardt [22] and Neuberg [23]. A summary of recent literature reports on bidentate phosphine ligands bound to solid supports can be found in Neuberg's thesis [23], in which the preparation of an active and stable cationic rhodium catalyst bound to silica via a chelating phosphine viz. $NBDRhL_2^+$ (L_2 = bis(diphenylphosphino)maleimide (Fig. 1)) is also reported. We have previously studied the use of cationic phosphinerhodium complexes viz. $[RhNBDL_2]^+ [ClO_4]^-$ for the catalytic hydrogenation of fatty oils [24]. In a further study of the cationic rhodium catalysts, we have tried to use the same ligand bound to silica. Our experience so far, however, has been disappointing; our silica bound complexes are usually stable in respect to metal particle formation (no colour change is observed), but unfortunately are also inactive. An obvious reason for the lack of activity is the presence of undesired ligands on the gel such as free amine groups, amidic acids and free surface hydroxyls. These groups, formed during the preparation of the gel, can act as catalyst poisons by blocking vacant coordination sites.

The present study had two aims. Firstly we sought a route by which undesired ligand sites on the surface can be avoided or minimized. Secondly we sought ways of proving the existence of potential ligand sites on the silica surface, which is not an easy task. Because of the very low concentration of such sites on the surface normal analytical and spectroscopic techniques are often not very informative [25], and so we used various IR probes. By treating metal carbonyl complexes with the functionalized gels, the nature of the ligand sites can be inferred from the infrared spectra of the resulting gels. This method has been frequently used in the past [26–29]. The bound metal carbonyl complexes are of interest in themselves besides being valuable infrared probes; Bailey and Langer [12] mentioned no Group VI metal carbonyl complexes containing bidentate ligands bound to silica and so the complexes prepared in the present study may have some novelty value.

Experimental

Materials

Analytical grade solvents were used throughout this work without further purifi-

cation. The metal carbonyls were purchased from Alfa Ventron Chemicals. 3-Aminopropyltriethoxysilane (AMEO) (a gift from Dynamit Nobel, West Germany), was vacuum distilled before use. The silica gel used (Kieselgel 200) was purchased from Merck and purified by repeated washings with concentrated HCl followed by thorough washings with distilled water and finally drying in vacuum at 135°C.

Bis(diphenylphosphino)maleic acid anhydride (BDMA) was synthesized as described by Fenske et al. [30]. $Mo(CO)_4NDB$ [31], $M(CO)_4(Pyridine)_2$ [32] and $[M(CO)_5Cl]PPh_4$ [33] (M = Cr, Mo, W) were prepared by published methods. All syntheses and other manipulations were carried out under dry argon. UV irradiations were carried out with an 150W Hanau high-pressure mercury lamp equipped with a quarz cooling jacket.

Infrared spectra

Infrared spectra were recorded with a Perkin–Elmer 580 infrared spectrometer equipped with a PE data station. The phosphinated silica gel was examined as KBr pellets and the immobilized metal carbonyls as Nujol mulls.

Analyses

C, H, N elementary analyses were carried out at the Microanalytical laboratory, University of Lund. The phosphorus content was determined as described by Hershcovitz et al. [34]. For confirmatory determinations we used the iodine method of Bartholin et al. [19] except that the excess iodine was determined spectrophotochemically. The analytical results for the phosphinated silica gels are listed in Table 1.

Preparation of phosphinated silica gels

Route 1. The aminated silica was prepared as described by Allum et al. [13]. 10 g aminosilica was suspended in 150 ml toluene. 5.1 g bis(diphenylphosphino)maleic acid anhydride and 100 μl pyridine where then added. The suspension was stirred at 60°C overnight. The reaction vessel was then equipped with a Dean–Stark apparatus and heated under reflux for 8 h then the suspension was filtered. The isolated solid was extracted with toluene for 12 h in a Soxhlet apparatus and finally dried in vacuo. This gel is subsequently referred to as P2I(1).

Route 2. 0.56 g bis(diphenylphosphino)maleic acid anhydride was dissolved in 100 ml degassed THF. To this solution 0.17 ml freshly distilled 3-aminopropyltriethoxylsilane was added. The colour then changed from dark red-orange to yellow-orange. After 2 h stirring at room temperature 1.2 g dry silica gel 200 was added and the slurry was stirred for 12 h, during which the colour changed to dark

TABLE 1

ANALYTICAL DATA

	P(%)	N(%)	mmol bisphosphine / mmol N
P2I(1)	0.64	0.34	0.42
P2I(2)	1.75	0.40	0.98
Aminosilica	–	0.46	–

red. 100 ml toluene was added and the reaction vessel was equipped with a Dean–Stark apparatus and heated under reflux for 8 h, after which the mixture was filtered. The isolated orange gel was washed with several portions of THF, toluene, acetone and finally dried in vacuum at 30°C. This phosphinated silica gel is referred to as P2I(2). Analytical results are given in Table 1. IR(Nujol): 1703 cm^{-1} (s, ν(C=O)).

Preparation of immobilized metal carbonyls

A. Photochemical reaction. About 1 mmol of the metal carbonyl ($M(CO)_6$) was dissolved in 50 ml degassed THF. After careful purging with argon the solution was irradiated for 1 h, then 0.2 g of P2I(2) (0.056 mmol ligand) was added and the resulting suspension was irradiated for 2 h. The gel was filtered off and washed several times with THF and toluene and finally dried in a stream of argon.

B. Thermal reactions. A suspension of 0.2 g P2I(2) and 0.5 g $W(CO)_6$ in 75 ml *o*-xylene was refluxed for 2 h. After cooling the solid was filtered off and washed several times with *o*-xylene and toluene.

C. Ligand exchange reactions. 0.3 g P2I(2) and an excess of $M(CO)_5ClPPh_4$ or $M(CO)_4L_2$ was equilibrated in acetone or THF for 2–4 hours. The mixture was filtered and the product washed several times with acetone.

Results and discussion

Preparation of the silica supported phosphine ligands

Reactions of hydroxyl groups on oxide surfaces with silylating agents, e.g. alkoxysilanes ($(RO)_3$–Si–R′) or halosilanes (X_3–Si–R′), do not fully remove all the hydroxyl groups on the surface [2,3]. Moreover the location of these hydroxyl groups is such that some unreacted alkoxy groups will remain [4] (Fig. 2). These unreacted hydroxy and alkoxy groups probably show little tendency to interact with a metal complex, but on treatment with aminoalkyltriethoxysilanes the hydroxyl groups might cause complications. Hydrogen bonding between surface bonded amine groups and hydroxyl groups [4] or between adjacent amine groups [35] will influence the likelihood of further reactions of the amine group (Scheme 1); even weak hydrogen bonding will make some of the amine groups inaccessible. The surface topology might increase this effect. Thus, as determined by ESCA [4]) only 6–27% of a propylamine modified SnO_2 surface could be brought into reaction with 3,5-nitrobenzoyl chloride to yield the desired surface bonded amide. Other investigators [36] have found, that only 20–50% conversion of bound amine groups can be achieved on silica gel surfaces.

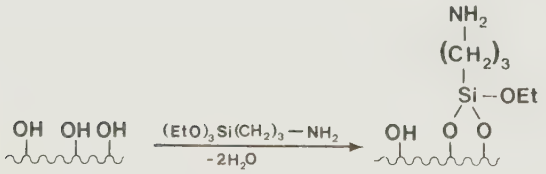
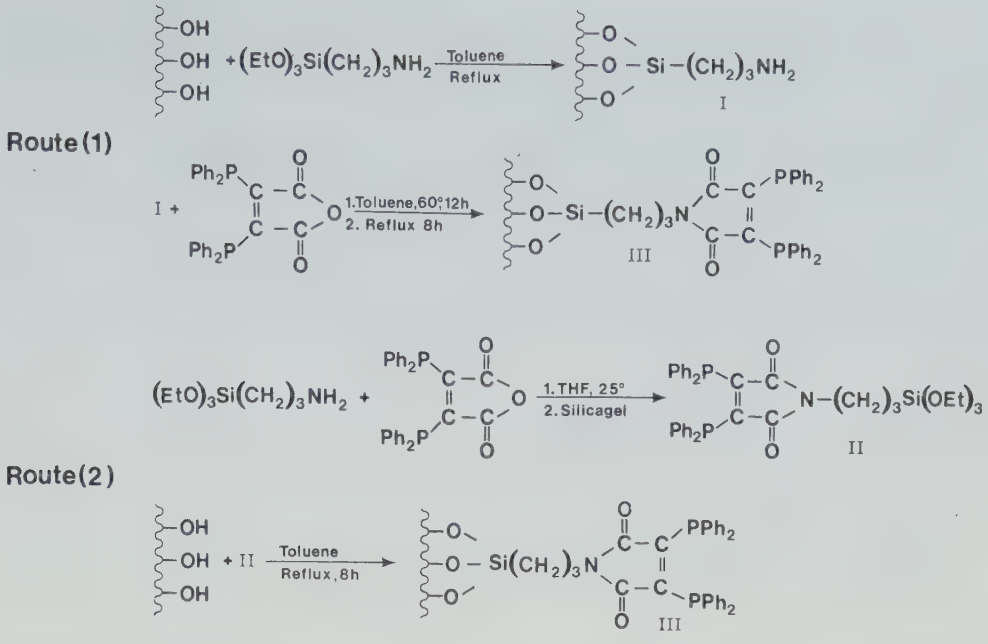


Fig. 2. Reaction of 3-aminopropyltriethoxysilane with surface hydroxyls on silica gel. Unreacted hydroxyls present on the surface.



SCHEME 1. Reaction sequences and conditions for the two preparative methods studied.

In Scheme 1 two different routes for the preparation of the silica-bound chelating ligand bis(diphenylphosphino)maleimide are outlined. Route 1 uses the traditional way of modifying silica surfaces, but in the present study only 42% (Table 1) of the surface bonded amine groups could be brought into reaction by this method; this is the highest figure we have reached and close to that observed by Neuberg (43–46%) [23], and in accord with the results in the similiar systems discussed above. The resulting silica gel thus contains two different ligand sites, viz. bidentate phosphine groups and amine groups.

In contrast, route 2 leaves almost no amine groups on the resulting gel. The principal difference between the two routes (Scheme 1) is the reaction sequence. To avoid reaction between the anhydride and the amine on the silica surface, this condensation was instead carried out in solution, where all the reactants are fully mobile and accessible for reaction. The imide II was then, without isolation, condensed on to the silica surface. To shift the equilibrium towards the imide site (II, Scheme 1) we used a 50% excess of the anhydride and carefully dried silica gel as the dehydrating agent. To avoid reactions of the ethoxy group on the 3-aminopropyltriethoxysilane it is important even at this stage to work under rigorously anhydrous conditions and to use freshly distilled organosilane, otherwise small primary particles of polymerized silane may form and they may contain amine groups inaccessible for further reaction with the anhydride. In the next step of the reaction (Scheme 1) this prepolymer can be condensed onto the silica surface. Provided that these careful steps are taken the preparation according to route 2 leads to a functionalized silica gel with only very small amounts of unreacted amine groups on the surface. This is shown by the ratio bisphosphine/nitrogen for the two preparations in Table 1. The increased incorporation of the phosphinomaleic unit in

TABLE 2

INFRARED STRETCHING FREQUENCIES IN THE ν(C–O) REGION FOR PREPARED SILICA-BOUND COMPLEXES AND REFERENCE COMPOUNDS

Metal	Preparation [a] method	Ligand [b]	ν(CO) frequencies (cm^{-1})					Medium	Ref.
Cr	1	P2I(1)	2063(w)	2015(m)	1981(m)	1937(s)	1895(s)	Nujol	This work
Mo	1,3	P2I(1)	2072(w)	2025(m)	1985(m)	1944(s)	1907(s)	Nujol	This work
W	1	P2I(1)	2067(w)	2020(m)	1979(m)	1930(s)	1900(s)	Nujol	This work
Cr	1,3	P2I(2)	2015(m)	1934(s)	1900(vs)			Nujol	This work
Mo	1,2,3	P2I(2)	2027(m)	1939(s)	1909(vs)			Nujol	This work
W	1,2,3	P2I(2)	2023(m)	1932(s)	1902(vs)			Nujol	This work
Cr	2	CHA	2067	1980	1935	1890		$CHCl_3$	32
Cr	2	BPE	2018	1932	1907			CS_2	40
Cr	1	BDMA	2021(m)	1937(m)	1910(s)			CCl_4	30
Mo	2	CHA	2072	1983	1938	1895		$CHCl_3$	32
Mo	2	BPE	2028	1937	1915			CS_2	40
Mo	3	BDMA	2031(m)	1947(m)	1924(s)			CCl_4	30
Mo	3	BDMM	2026	1922	1910	1890		$CDCl_3$	41
W	2	CHA	2071	1974	1929	1894		$CHCl_3$	32
W	2	BPE	2024	1930	1907			CS_2	40
W	1	BDMA	2028(m)	1940(m)	1916(s)			CCl_4	30

[a] 1 = photochemical, 2 = thermal, 3 = ligand exchange. [b] CHA = cyclohexylamine, BPE = bis(diphenylphosphino)ethylene, BDMA = bis(diphenylphosphino)maleic acid anhydride, BDMM = bis(diphenylphosphino)maleimide.

P2I(2) at the same amine loading as in P2I(1) is also apperent from the IR absorption intensities of the C=O stretching vibration of the imide (II, Scheme 1) at 1703 cm^{-1}.

As discussed above one possible reason for the low conversion of amine groups on a silica surface is hydrogen bonding. Moses et al. raised the question whether the metal ions are effective in disrupting such hydrogen-bonded amine structures [4], but found no answer in their study. However, if metal ions can coordinate to hydrogen-bonded amine sites, a gel functionalized according to route 1 (Scheme 1) will most probably seriously effect the chemical behaviour of metal complexes bound to it. It is thus important to assay potential metal interacting groups. To do this we used metal carbonyls as the reacting metal species.

Reactions of the silica supported ligands with metal carbonyl complexes

Group VI e.g. Cr, Mo, W hexacarbonyl complexes are known to react with many Lewis bases such as amines [32] or phosphines [30] to yield the corresponding $M(CO)_{6-x}L_x$ complexes. The reaction can be carried out in different ways, e.g. thermally, photolytically (eq. 1) or via the replacement of a less strongly bonded ligand (eq. 2). If such reactions are used to assay potential ligands on a solid surface, the product formed should be independent of the method of preparation and, above all, it should depend on the type of ligands present.

eq.1 $$M(CO)_6 + L \xrightarrow[\text{or heat}]{h\nu} M(CO)_{6-x}L_x + xCO$$

eq.2 $$M(CO)_{6-x}Y_x + L \longrightarrow M(CO)_{6-z}L_z + xY$$

eq.3 $$M(CO)_5X^- \xrightarrow[K_1]{L} M(CO)_4LX^- + CO \xrightarrow[K_2]{L} M(CO)_4L_2 + X$$

eq.4 $$M(CO)_5X^- \xrightarrow[K_3]{L} M(CO)_5L + X^-$$

The photolytic reaction (eq. 1), is a rather specific reaction and the amine groups which take part in this reaction may not react under other conditions. Thus we have supplemented the photolytic reaction by using the very mild ligand-substitution route of equation 2 (Y = norbornadiene). The observed formation of a $Mo(CO)_5$-amine complex (Table 2) for both reactions shows the existence of amine groups on P2I(1) which although inaccessible for further reaction with anhydride can coordinate metal atoms.

One other feature of the reaction of P2I(1) with $Mo(CO)_4$NBD should be noted. The dissociation of the NBD ligand will leave two vacant coordination sites on the metal atom, and so the bidentate phosphine might easily form a *cis*-chelating bisphosphine complex. Such a complex is actually observed (Table 2). An isolated amine group on the gel, on the other hand, could lead to one of the hypothetical tetracarbonyl complexes in Fig. 3, but no such products were observed (Table 2). Instead we found the pentacarbonylamine complex, and evidently the vacant metal

site is filled by a CO ligand. As no extra CO was added in the preparation, the CO incorporated is probably derived from some kind of decomposition of the neighbouring carbonyl complexes. Similar decompositions have been observed in

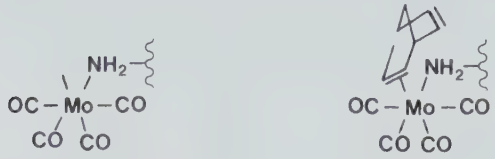


Fig. 3. Two possible substitution products from reaction of $Mo(CO)_4NBD$ with surface bound amine groups.

other studies concerning carbonyl complexes on solid carriers [38,39], but no mechanism for the reaction has been suggested.

In Table 2 we list the infrared CO frequencies of the species we have prepared together with those for some selected reference compounds. For all our preparations from the P2I(1) gel the general spectral pattern observed (Fig. 4) is the same. It is rather complex but can be analysed in terms of two superimposed spectra of the two species present viz. the pentacarbonylamine complex and the tetracarbonylbis-chelating-phosphine complex. The bands of highest diagnostic value [37] are the $M(CO)_5$-amine A_1 mode at ≈ 2070 cm^{-1} (w), and the $M(CO)_4$(P2I) A_1 mode at ≈ 2020 cm^{-1} (m). Many bands below 2000 cm^{-1} tend to coincide, but all the bands can nevertheless be seen more or less clearly.

For comparison we treated the molybdenum carbonyl with an aminated silica gel (not further treated with BDMA). The spectrum obtained for this preparation is in excellent agreement with our assignment of the pentacarbonylmonoamine bands in the other preparations viz. 2072 cm^{-1} (w), 1985 cm^{-1} (m), 1941 cm^{-1} (s), 1910 cm^{-1} (w,sh).

It is evident that the P2I(1) gel contains two different potential ligand groups. Both of these ligands can undoubtedly bind metal ions. The assumed hydrogen bonding of the amine groups does not prevent them taking part in metal coordination. The IR spectra of the product gels made from P2I(2) are clean and simple, showing only the pattern characteristic of a *cis*-$M(CO)_4L_2$ complex (Fig. 5). No trace of aminepentacarbonyl species are found. The positions of the bands are also in very good agreement with those found for similar soluble complexes (Table 2). Hence route 2 in Scheme 1 makes it possible to prepare a silica gel bearing the desired chelating bisphosphine as the sole metal binding group.

In addition to the two methods used to bring P2I(1) into reaction with carbonyl complexes, photochemical reaction with $M(CO)_6$ and reaction with $M(CO)_4NBD$, we have for P2I(2) also used thermal reaction with $M(CO)_6$ and treatment with the anionic pentacarbonyl halide complex $M(CO)_5Cl^-$ PPh_4^+ (M = Cr, Mo, W); complexes of this latter type are known to react with donor ligands such as isonitriles [42], amines [43] and phosphines [44,45]. A number of different possible substitution products i.e. $M(CO)_5L$, $(M(CO)_4XL)^-$ and $M(CO)_4L_2$ complexes can be obtained depending on donor ligand, halide and solvent. Allen and Barret [45] report $K_1 \gg K_3$ for monodentate phosphines in the case of M = Cr, Mo and X = Cl, but $K_1 \approx K_3$ for M = W, X = Cl (eq. 3 and eq. 4). In our preparations, regardless of

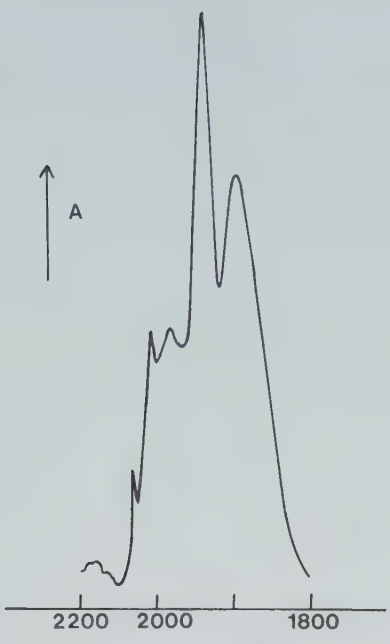


Fig. 4. IR spectrum in the CO stretching region of P2I(1) treated with $Cr(CO)_6$.

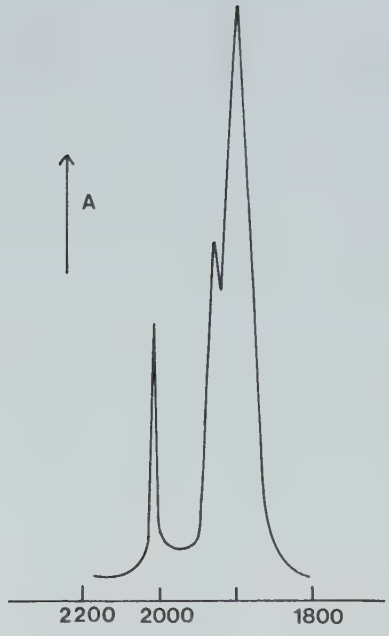


Fig. 5. IR spectrum in the CO stretching region of P2I(2) treated with $Cr(CO)_6$.

metal, we have found no evidence for any monosubstituted products, i.e. no $M(CO)_4XL^-$ complex or $M(CO)_5L$ (Table 2). For Cr and Mo this can be explained in terms of the reported rate constants [45] and the strong chelate effect of the phosphine used in our study. Once the kinetically favoured $M(CO)_4XL^-$ complex is formed it will react to form the observed bisphosphine complex because of the close proximity of the other phosphine group on the ligand. For W, on the other hand, on the basis of the same kinetic evidence [45] a mixture of the two complexes viz. $W(CO)_4LX^-$ and $W(CO)_5L$ would be expected, but the chelate effect will probably result in the formation of the bisphosphine complex from both these complexes. A product pattern in agreement with that expected on kinetic grounds i.e. $M(CO)_5L$ and $M(CO)_4L_2$ for Cr and Mo and for W also $W(CO)_4ClL^-$ was observed by Menzel et al. [38] in their study of polystyrene bound isonitrile ligands. This can be taken as a support for our assumption above that the reaction rates K_1, K_2, and K_3 (eq. 3 and 4) are not greatly altered by the use of matrix bound ligands, and thus the product pattern we have found is mainly due to the strong chelating effect of our ligand.

In the present study we have investigated potential ligand sites on silica gel by using carbonyl complexes as IR probes. Provided that the reacting complexes are carefully choosen much information can be gained this way. We are at present continuing our study with the aim of using silica systems as carriers for labile (i.e., catalytically active) as well as stable metal complexes.

Acknowledgements

We thank Dr. Baruch Yom-Tov for the skilfull preparation of the bis(diphenylphosphino)maleic acid anhydride. Financial support from Styrelsen för Teknisk

Utveckling (The Swedish Board for Technical Development) and from the Royal Physiographic Society in Lund (to C. Andersson and M. Berglund) is gratefully acknowledged.

References

1 K. Mosbach, FEBS Lett., 62 (1976) E80.
2 K.K. Unger, Porous Silica, Elsevier, New York. 1979.
3 R.E. Majors and M.J. Hopper, J. Chromatogr. Sci., 12 (1974) 767.
4 P.R. Moses, L.M. Wier, J.C. Lennox, J.R. Lehnard and R.W. Murray, Anal. Chem., 50 (1978) 576.
5 J. Lieto, D. Mistein, R.L. Albright, J.V. Minkiewicz and B.C. Gates, CHEMTECH., (1983) 46.
6 F.R. Hartley and P.N. Vezey, Adv. Organometal. Chem., 15 (1977) 189.
7 G. Manecke and W. Storck, Angew. Chem., 90 (1978) 691.
8 M. Scurell, Catalysis, Vol 2, p. 215, Chem. Soc., London, 1978.
9 D.D. Whitehurst, CHEMTECH., (1980) 44.
10 A.Y. Yuffa and G.V. Lisichkin, Russ. Chem. Rev., 47 (1978) 751.
11 F. Ciardelli, G. Braca, C. Carlini, G. Sbrana and G. Valentini, J. Mol. Cat., 14 (1982) 1.
12 D.C. Baily and S.H. Langer, Chem. Rev., 8 (1981) 104.
13 K.G. Allum, R.D. Hancock, I.V. Howell, S. McKenzie, R.C. Pitkethly and P.J. Robinson, J. Organomet. Chem., 87 (1975) 203.
14 K.G. Allum, R.D. Hancock, I.V. Howell, T.E. Lester, S. McKenzie, R.C. Pitkethly and P.J. Robinson, J. Organomet. Chem., 107 (1976) 393.
15 A. DeMunck, M.W. Verbruggen and J.J.F. Scholten, J. Mol. Cat., 10 (1981) 313.
16 C.U. Pittman and A. Hirao, J. Org. Chem., 43 (1978) 640.
17 C. Andersson and R. Larsson, J. Catal., 81 (1983) 194.
18 F. Pinna, C. Candilera, G. Strukul, M. Bonivento and M. Graziani, J. Organomet. Chem., 159 (1978) 91.
19 M. Bartholin, C.H. Graillat, A. Guyot, G. Coudurier, J. Bandiera and C. Naccache, J. Mol. Cat., 3 (1977/78) 17.
20 R.D. Hancock, I.V. Howell, R.C. Pitkethly and P.J. Robinson, in B. Delmon, G. Jonnes (Eds,), Catalysis, Heterogeneous and Homogeneous, Elsevier, New York, 1975, p. 349.
21 R.S. Drago, E.D. Nyberg, A.Ei. A'mma and A. Zombeck, Inorg. Chem., 20 (1981) 641.
22 D.N. Marquardt, Ph.D. Thesis, Stanford University (USA), 1974.
23 M.K. Neuberg, Ph.D. Thesis, Stanford University (USA), 1978.
24 C. Andersson and R. Larsson, J. Am. Oil Chem. Soc., 58 (1981) 54.
25 J.P. Collman and L.S. Hegedus, Principles and Applications of Organotransition Metal Chemistry, University Science Books, 1980, chapter 6.
26 A.R. Sanger and L.R. Schallig, J. Mol. Cat., 3 (1977/78) 101.
27 B. Rebenstorf and R. Larsson, Z. Anorg. Allg. Chem., 478 (1981) 119.
28 B. Rebenstorf and R. Larsson, J. Mol. Cat., 11 (1981) 247.
29 C. Andersson and R. Larsson, J. Catal., in press.
30 D. Fenske and H.J. Becher, Chem. Ber., 107 (1974) 117.
31 M.A. Bennet, L. Prah and G. Wilkinson, J. Chem. Soc., (1961) 2037.
32 C.S. Kraihanzel and F.A. Cotton, Inorg. Chem., 2 (1963) 53.
33 E.W. Abel, J.S. Butler and J.G. Reid, J. Chem. Soc., (1963) 2068.
34 H. Hershcovitz and G. Schmuckler, J. Inorg. Nucl. Chem., 41 (1979) 687.
35 S. Shinoda and Y. Saito, Inorg. Chim. Acta, 63 (1982) 23.
36 H. Engelhardt and D. Mathes, J. Chromatogr., 142 (1977) 311.
37 D.M. Adams, Metal–Ligand and Related Vibrations, Edward Arnold Publishers Ltd London, 1967, chapter 3.
38 H. Mentzel, W.P. Fehlhammer and W. Beck, Z. Naturforsch. B, 37 (1982) 201.
39 C. Andersson, R. Larsson and B. Yom-Tov, Inorg. Chim. Acta, 76 (1983) L185.
40 R.T. Jernigan, R.A. Brown and G.R. Dobson, J. Coord. Chem., 2 (1972) 47.
41 D. Fenske and H.J. Becher, Chem. Ber., 108 (1975) 2115.
42 H.D. Murdoch and R. Henzi, J. Organomet. Chem., 5 (1966) 166.
43 H.D. Murdoch and R. Henzi, J. Organomet. Chem., 5 (1966) 463.
44 A.D. Allen and P.F. Barrett, Can. J. Chem., 46 (1968) 1649.
45 A.D. Allen and P.F. Barrett, Can. J. Chem., 46 (1968) 1655.

II

Hydrogenation of Soybean Oil with Cationic Rh(I)-Phosphine Complexes as Catalysts – Para-Toluene Sulfonate and Sulfonated Styrene Resins as Counterions

MATS BERGLUND and **CARLAXEL ANDERSSON**, Inorganic Chemistry 1, Chemical Center, P.O.B. 740, S-220 07 Lund, Sweden

ABSTRACT

A cationic rhodium(I) complex, viz. Rh NBD diphos$^+$ 4-CH_3-$C_6H_5SO_3^-$ [NBD = norbornadiene, diphos = $(C_6H_5)_2$ P-CH_2-CH_2-$P(C_6H_5)_2$], has been used as a homogeneous catalyst for the hydrogenation of soybean oil in acetone solution. This complex acts almost in the same way as the corresponding ones with ClO_4^- or PF_6^- as counterions, i.e., it gives high polyene selectivity and low formation of *trans* isomers. Because of the somewhat stronger basic character of the p-toluene-sulfonate ion compared with the perchlorate and hexafluorphosphate ions, the relative proportion of reaction via the so-called monohydride path is larger in the present case. When the ionic complex, Rh NBD diphos$^+$, is bound to a solid support, e.g., to the anionic sites of sulfonated polystyrene resins, a nearly total lack of catalytic activity is observed. Possible reasons for these effects are discussed in terms of π-arene-metal binding and covalent coordination of the sulfonate group.

INTRODUCTION

The rather unique properties of cationic rhodium complexes, e.g., NBD Rh L_2^+ X^- where NBD = norbornadiene, L = tertiary phosphine and X = ClO_4^- or PF_6^-, as catalysts for the hydrogenation of olefins are now well documented (1-4). These types of complexes have shown high polyene selectivity and a low formation of *trans* isomers in the hydrogenation of fatty acid methyl esters (5) and triglycerides (6). For practical applications, however, the catalysts must be separated easily from the reaction mixture and also easy to reuse. This possibly can be achieved by using one of the techniques to bind transition metal complexes to solid carriers that have been reported in recent years. This can be done via covalent (7-9) or ionic interactions (10-12). Attempts to immobilize the present type of complexes to phosphinated polystyrene resins also have been published (13-15). These matrix-bound complexes tend, however, to be unstable under hydrogenation conditions and are reduced to the metallic state (15-16).

To improve catalyst stability, Neuberg (17) has developed a silica-bound chelating bisphosphine ligand. The complexes prepared with this new ligand are reported (17) to be active and stable with essentially the same characteristics as those of the homogeneous analog.

In the present communication we report our attempts to use a matrix-bound counterion, O-X^-, to immobilize the cationic complex. The ion X^- chosen for this study was the sulfonate group -R-SO_3^- in commercially available anion exchangers.

A preliminary study was carried out in a homogeneous stystem with p-toluenesulfonate as the anion. During the course of this work a brief note (18) on similar studies was reported.

EXPERIMENTAL

Two different substrates were tested, 1-hexene and soybean oil. Analytical and hydrogenation procedures were the same as reported previously (6).

Preparation of Rhodium Complexes

Rh NBD diphos$^+$ 4-$CH_3C_6H_4SO_3^-$ was prepared by reacting Rh NBD acetylacetonate (acac) with p-toluene sulfonic acid (1 equ.) and subsequently with diphos (1 equ.) in tetrahydrofuran solution (19). An orange-red crystalline compound precipitated when diethylether (Rh = 13.4%) was added. To prepare the polymer-bound complex, the following procedure was used. The strongly acid macroreticular resin, Amberlyst XN-1010 (surface area 540 m^2/g, ion exchange capacity 3.3 meq/g), was purified by washing with NaOH (1 M) , HCl (1 M), distilled water, acetone and toluene in this order. It was extracted with methanol for 18 hr and dried under vacuum (1 torr, 50 C) for 6 hr. Rh NBD diphos$^+$ ClO_4^- (150 mg) in acetone solution was then reacted with the resin (500 mg). These amounts correspond to a ratio -RSO^3H/Rh of 8/1, i.e., one is not making use of the full ion exchange capacity. In this way a complete decoloration of the acetone solution was reached, yielding a gel with 3.6% Rh.

RESULTS AND DISCUSSION

Homogeneous System

In a hydrogenation experiment with the complex Rh NBD diphos$^+$ $-$-4-CH_3-C_6H_4-SO_3^-, the product composition is shown as a function of the iodine value in Figure 1. This pattern is qualitatively the same as that found previously (6) with the complex Rh NBD diphos$^+$ ClO_4^- and triethylamine added, i.e., a very low increase in stearate and a rather high increase in *trans* and conjugated isomers with decreasing iodine value. This result is probably an effect of the basicity of the p-toluene sulfonate group in acetone media. By its proton affinity (eq. 3) the sulfonate ion shifts the equilibrium 2 towards the monohydride side.

$$\text{NBD Rh diphos}^+ + H_2 \rightarrow \underset{\text{(I)}}{\text{Rh diphos } H_2^+} \qquad [1]$$

$$\text{Rh diphos } H_2^+ \rightleftarrows \underset{\text{(II)}}{\text{Rh diphos H}} + H^+ \qquad [2]$$

$$-RSO_3H \rightleftarrows RSO_3^- + H^+ \qquad [3]$$

The monohydride (II) is known to be an effective catalyst of hydrogenation and isomerization (1). The presence of this complex will, therefore, produce hydrogenated as well as isomerized products as found.

Addition of $HClO_4$ (3 equ.) to the same reaction mixture as above results in a different product pattern (Fig. 2). In this case the amount of undesirable products, e.g., *trans* and conjugated isomers, is reduced considerably. Probably the added acid shifts equilibria 2 and 3 to their left-hand side. Therefore, a reaction via the dihydride Rh diphos H_2^+ occurs, giving lower amounts of isomerized products. Even in this case, however, the monohydride complex is probably also operating, but to a much lower extent.

Heterogeneous System

We now turn to the case where the sulfonate group is bound to an organic polymer. The position of the equi-

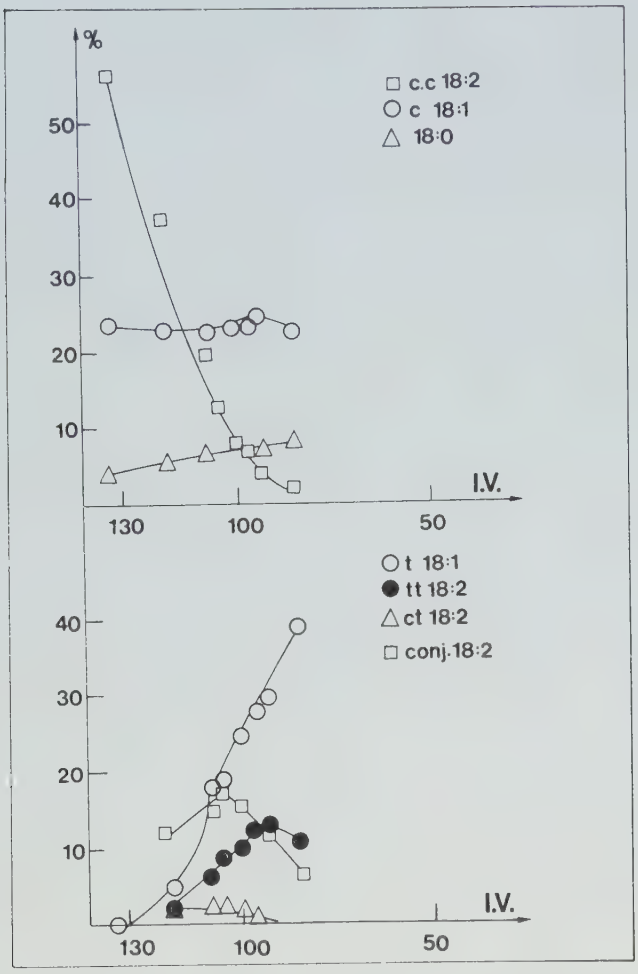


FIG. 1. Product composition at different iodine values in the hydrogenation of soybean oil (1.0 mL) with Rh NBD diphos$^+$ 4-CH_3-C_6H_4-SO_3^- (58 mg) as catalyst. Methyl linolenate (7.8%) in the starting oil was not detected further as reaction progressed. Acetone solution (9 mL), total pressure 1 atm. and temperature T = 31 C. No additives.

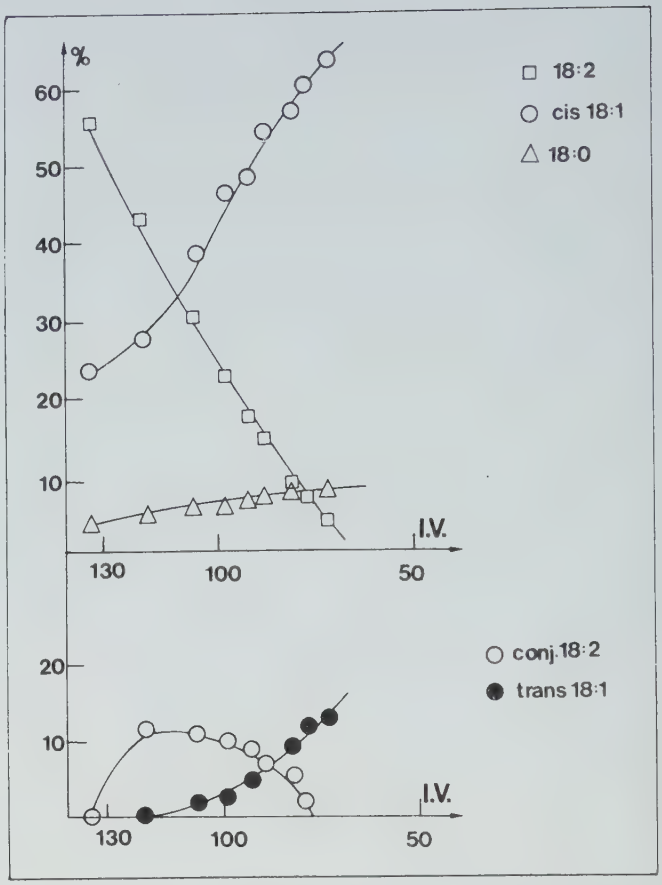


FIG. 2. Product composition at different iodine values with $HClO_4$ added to the reaction mixture. Conditions as in Figure 1; [$HClO_4$] = 20 mM.

librium in eq. 2 can then be controlled by having only a part of the available sulfonate groups in the gel exchanged for the rhodium complex, whereas the main part is in the acidic form (eq. 3). Hence, controlling the extent of isomerization should be possible. One must, however, be careful not to protonate all the sulfonate groups in the resin. This would make the electrostatic binding of the positive Rh-complex impossible.

For the reasons given above we have used acidic groups in the resin, i.e., a high sulfonate to rhodium ratio. All catalysts prepared in this way were found to be inactive for soybean oil hydrogenations. The only case where very low activity has been observed is for the hydrogenation of 1-hexene.

Because the small-sized substrate 1-hexene also gives a very low rate of reaction compared with the homogeneous counterpart (1), the lack of activity observed for soybean oil samples is probably not caused by mass transport limitations inside the polymer gel. The main difference between the homogeneous system NBD Rh diphos$^+$ -p-toluensulfonate and its heterogeneous counterpart is the ratio of Rh to sulfonate groups and π-arene groups. In the homogeneous system, one arene group and one sulfonate group occurs for every rhodium atom whereas in the heterogeneous system, the R-SO_3/Rh ratio is 8 and the arene/Rh ratio is even greater. These groups might have a greater possibility in the heterogeneous system to block the metal center and result in an inactive complex. Evidence for sulfonate coordination via oxygen binding to rhodium has been published recently (18,20). We, too, have observed during the present study that the addition of excess p-toluensulfonic acid to the homogeneous system inhibits its catalytic activity completely. π-Arene coordination to rhodium also is well documented (4,21-22).

Results from the present investigations on the homogeneous and the matrix-bound systems indicate that if the ionic binding approach is to be applied successfully nonaromatic polymers with ionic groups less basic than the sulfonate group must be used.

REFERENCES

1. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 98:2134 (1976).
2. Schrock, R.R., and J.A. Osborn, Ibid. 98:2143 (1976).
3. Schrock, R.R., and J.A. Osborn, Ibid. 98:4450 (1976).
4. Halpern, J., A.S.C. Chan, D.P. Riley and J.J. Pluth, Adv. Chem. Ser. 173:16 (1979).
5. van der plank, P., A. van der Ent, A.L. Ondelinden and H.J. Van Oosten, JAOCS 57:343 (1980).
6. Andersson, C., and R. Larsson, JAOCS 58:54 (1981).
7. Hartley, F.R., and P.N. Vezey, Adv. Organomet. Chem. 15:189 (1977).
8. Lieto, J., D. Milstein, R.L. Albright, J.V. Minkiewicz and B.C. Gates, Chemtech 1:46 (1983).
9. Whitehurst, D.D., Ibid. 1:44 (1980).
10. Haag, W.O., and D.D. Whitehurst, Ger., Offen. 1, 800, 380; Ger., Offen. 1, 800, 371; Ger., Offen. 1, 800, 379.
11. Tang, C.S., T.E. Paxson and L. Kim, J. Mol. Cat. 9:313 (1980).

12. Pinnavaia, T.J., R. Raythatha, J. G.-S. Lee, L.J. Halloran and J.F. Hoffman, J. Am. Chem. Soc. 101:6891 (1979).
13. Graziani, M., G. Strukul, M. Bonivento, F. Pinna, E. Cernia and N. Palladino, in Catalysis, Heterogeneous and Homogeneous, B. Delmon and G. Jannes, eds., Elsevier Scientific Publishing Co., New York, 1975, 331-337.
14. Strukul, G., M. Bonivento, M. Graziani, E. Cernia and N. Palladino, Inorg. Chem. Acta 12:15 (1975).
15. Pinna, F., C. Candilera, G. Strukul, M. Bonivento and M. Graziani, J. Organomet. Chem. 159:91 (1978).
16. Andersson, C., M. Berglund and R. Larsson, Progress Report, Swedish Board for Technical Development STU 80-3706, 1981.
17. Neuberg, M.K., Thesis, Stanford University, 1979.
18. Reiss, J., V. Vaisarová and J. Hetflejš, XXII International Conference on Coordination Chem., Budapest, Hungary, Aug. 23-27, 1982, Abstract no. Fr. P. 18.
19. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 93:2397 (1971).
20. Borowski, A.F., D.J. Cole-Hamilton and G. Wilkinson, Nouveau Journal de Chimie 2:137 (1978).
21. Schrock, R.R., and J.A. Osborn, J. Am. Chem. Soc. 93:3089 (1971).
22. Cole-Hamilton, D.J., R.J. Young and G. Wilkinson, J.C.S. Dalton 1995 (1976).

[Received January 9, 1984]

III

Polar organic polymer as catalyst support in the olefine metathesis reaction

Mats Berglund and Carlaxel Andersson

Research group on catalysis, Inorganic Chemistry 1
Chemical Center, University of Lund, P.O.B. 124
S-221 00 LUND, Sweden

Proof and correspondence to

Mats Berglund

Research group on catalysis, Inorganic Chemistry 1
Chemical Center, University of Lund, P.O.B. 124
S-221 00 LUND, Sweden

Summary.

The metathesis of Z-2-pentene has been studied using $Mo(NO)_2L_2Cl_2$ immobilized on a polar organic polymer, viz. a co-polymer of hydroxyethylmethacrylate and ethylene dimethacrylate, as the catalyst. Substitution of the pyridine ligands in $Mo(NO)_2(pyridine)_2Cl_2$ with the polymer-bound ligands has been found to give the most stable catalyst.

The cocatalyst $EtAlCl_2$ has been found to interact with the polar functional groups on the polymer causing a relatively high consumption of co-catalyst. The reaction of the polar groups with $EtAlCl_2$ has been mimiced in a separate study in which $Mo(NO)_2(PPh_3)_2Cl_2$ was used as the catalyst and with methylstearate added to the reaction medium.

For the polymer- bound catalyst the activity and the stereoselectivity at 0% conversion has been found to be almost identical to that observed for homogeneous analouges.

Introduction

The method of metal complex immobilization on solid support e.g. polystyrene is today a well established technique [1,2]. Applied to the type of catalyst systems used in the olefin metathesis reaction two different approaches have emerged viz. immobilization of the catalyst precursor (A) and immobilization of the co-catalyst (B). Reported examples of method A have used phosphine [3] or bipyridine ligand [4] bound to the support. These ligands were then in turn used to covalently bind a transition metal complex e.g. $M(CO)_{6-x}L_x$ (M = Mo,W L=polymer bound ligand). Addition of co-catalyst then gave an active catalyst. By the use of method B the catalyst precursor is linked to the support via reaction with the polymer bound co-catalyst and simultaneously activated. Reported examples of this method includes WCl_6 and as the polymer bound co-catalyst either $EtAlCl_2$ [5] or $SnMe_4$ [6]. Method A is restricted to complexes bearing ligands that can easily be linked to a support. This means that complexes like WCl_6 co-ordinated solely to chloro ligands can not be immobilized via this route. In addition, in order to prevent servere metal-leaching from the support, the bond between the metal and the supported ligand must be chemically stable under the catalytic cycle.

One metal complex highly active as catalyst for metathesis of olefines and which can meet the two requirements mentioned is the $Mo(NO)_2L_2Cl_2$ (M = Mo, W) type of complexes. These complexes were originally introduced as metathesis catalysts by Zuech et.al. [7] and further explored by Hughes [9]. The ligands denoted L in the formula can be phosphines, phosphites, amines i.e. ligands that with traditional methods can be bound to a support. Moreover earlier reports [8, 9] indicate that the Mo-L linkage is stable under catalyst

generation (treatment with co-catalyst) as well as under the catalytic cycle. However, whether the active specie is ligated by or free from the ligand L is a matter of controversy since in a recent investigation Seyferth et.al. [10] formulated an active intermediate as a MoCl(NO) fragment free from the ligand L.

Immobilization of $Mo(NO)_2L_2Cl_2$ on phosphinated polystyrene have been described by Grubbs et.al. [6]. They found that after activation with $Me_3Al_2Cl_3$ this gave nearly the same activity as the non-supported complex. No information on metal-leakage was, however, reported in that study.

In the present study we report results on the metathesis of olefines with $Mo(NO)_2L_2Cl_2$ supported on a different type of polymer gel viz. a co-polymer of hydroxyethylmethacrylate and ethylendimetacrylate (Fig. 1). To our knowledge this is the first study in which a highly polar organic polymer is used as a support for homogeneous metathesis catalysts. Since it is well known that the presence of Lewis-bases inhibit or diminish the activity for most metathesis catalyst systems, our results with this polar carrier can be related to the problem of metathesis of functionalized olefines, vide supra, the metathesis of 2-pentene in the presence of methylstearate.

Experimental

Materials

Z-2-pentene was purchased from Fluka and stored as received over activated molecular sieves. Analytical grade chlorobenzene was dried over CaH_2 and destilled under nitrogen before use. $EtAlCl_2$ (Alfa Ventron) was used as received and diluted to the desired

concentration with dry oxygen-free chlorobenzene under nitrogen. The polymer Spheron 1000 was purchased from Lachema, Czechoslovakia. Before use, the polymer was washed with aceton, methanol, dichloromethane and finally dried in vacuuo. $Mo(NO)_2Cl_2$ and $Mo(NO)_2L_2Cl_2$ (L = pyridine, triphenylphosphine, benzonitrile, diphenylbuthoxyphosphine) were prepared according to the procedures described by Cotton and Johnson [11].

All synthesis and manipulations were carried out under dry oxygen-free nitrogen.

Infrared spectra

Infrared spectra were recorded with a Perkin-Elmer 580B infrared spectrometer equipped with a PE data station. The polymers were examined as KBr or polyethylene pellets. Infrared determination of the complex formation between $EtAlCl_2$ and methylstearate was done as described earlier by Kemula et.al. [16].

Analysis

C, H, N elementary analysis were carried out at the Microanalytical laboratory, University of Lund. Molybdenum was determined by AAS. The analytical determination of phosphorous [12] and the number of hydroxyl groups [13] followed literature procedures. The reaction mixtures from the olefine metathesis experiments were analysed on a Perkin Elmer F17 GC equipped with a computing integrator (LCI-100). Two different columns were used viz. 10 % . TCEP on Chromosorb P and Durapak n-octane/Poracil C. The different products obtained were identified by mass spectrometry and by comparision of their retention times with that of authentic samples.

Preparation of polymer bound catalysts

The polymer was phosphitated by the method described by Gates et.al. [1] viz. esterfication of chlorodiphenylphosphine with the hydroxyethyl groups on the polymer in presence of pyridine as the base. By this method a polymer with 2.3 % phosphorous was prepared.

The catalyst precursor $Mo(NO)_2L_2Cl_2$ was immobilized by the two following routes.

Route 1. Ligand exchange

The phosphitated polymer was equilibrated in boiling CH_2Cl_2 with an excess of $Mo(NO)_2L_2Cl_2$ (L = pyridine or benzonitrile) for 4-5 h. The green-yellow polymer was filtered, Soxhlet extracted with CH_2Cl_2 for 16 h and finally dried in vacuuo.

Route 2. Reaction with $Mo(NO)_2Cl_2$

1.0 g phosphitated polymer was suspended in 50 ml of degassed CH_2Cl_2 and treated with 83 mg $Mo(NO)_2Cl_2$ for 18 h at room temperature. Filtration, Soxhlet extraction and drying gave a yellow-green polymer.

Analytical data for the prepared catalyst precursors are collected in Table 1.

Olefine metathesis experiments

The catalytic experiments were conducted in a 25 ml two-necked glass vessel equipped with a silicon rubber septum and connected to a tubing system which allowed the introduction of co-catalyst or chlorobenzene from storage bottles and nitrogen or vacuum via the

vacuum line. The glass vessel was dried in an oven at 130°C before use. After introduction of the desired amount of the polymer bound catalyst precursor the vessel was evacuated for 15 minutes and then filled with nitrogen. Thereafter 10 ml of chlorobenzene was introduced followed by the desired amount of $EtAlCl_2$ in chlorobenzene. Then the olefin was added and the pressure was adjusted to 1 atm. A similar procedure was also used with the corresponding non-supported complexes except that an induction period of 60 minutes was used in this case. Sampling was done with a hypodermic syringe via the membrane. The polymer bound catalyst was separated by centrifugating the samples. For the case of the homogeneous catalysts the reaction was terminated by addition of ethanol to the samples.

Initial rates expressed as mole substrate converted per minute and mole catalyst was calculated from the initial slopes of the conversion versus time curves.

Results and discussion

Catalyst preparation and characterisation

The synthesis of the polymer bound molybdenum complexes starts with the introduction of the phosphorous donor ligand on the polymer via reaction of the surface hydroxyls groups with chlorodiphenylphosphine (eq. 1). A theoretical value of 10 % phosphorous can be calculated using the number of hydroxyl groups on the polymer surface determined by titration (see experimental). The highest figures we have reached, however, is 2.3 % phosphorous corresponding to 23 % of the theoretical conversion. This shows that a large proportion of the surface hydroxyl groups are not accessible for reaction with chlorodiphenylphosphine under the condition used. Nevertheless under other conditions or together with other reagents

such surface hydroxyls are potentially reactive as discussed earlier [14]. In the esterfication reaction there is also a possibility for isomerisation to form a tertiary phosphine oxide on the surface [15].

The possibility of metal binding via hydroxyl and/or phosphine oxide groups must thus be taken into account in the preparation of the catalyst. These extra ligand sites and the complexes eventually formed from them will affect the catalytic behaviour and the stability of the catalyst.

With this in mind we have investigated two different ways to prepare our catalyst precursors. Starting from the polymeric molybdenum-nitrosyl compound (eq. 2) reactions with phosphines, phosphine oxide and alcohol hydroxyl groups [11, 17] have been observed. In the case of phosphines or phosphine oxides complexes of the $Mo(NO)_2L_2Cl_2$ type are obtained, while the alcohol complexes are less well-defined with the general formula $Mo(NO)_2Cl_2(ROH)_x$ [17]. Applying eq. 2 to the synthesis of polymer bound catalysts at least three different complexes can consequently be expected to form on the polymer. In addition, part of the polymeric nature of the starting complex can stay intact if the ligand sites on the polymer are well separated. These oligomers can under catalytic conditions split to form other complexes or eventually cause metal-leaching. To our opinion the ligand substitution reaction (eq. 3) is in this respect more attractive. In this case the ligands on the polymer have to compete with the exchanging ligand. The relative proportion of the different complexes formed on the polymeric resin will therefore be dependent on the relative amount of the different ligands and of their complexing ability compared to that of the leaving ligand.

After reaction of the pyridine complex with the non-phosphitated polymer the polymer was recovered unchanged, while reaction with the benzonitrile complex resulted in a substantial metal uptake as noted by the color of the polymer. In the infrared spectrum of this latter polymer no sign of any coordinated benzonitrile was observed, but the spectrum showed two bands in the NO-stretching region viz 1795 cm^{-1} and 1695 cm^{-1}. These frequencies are in accordance with those observed for alcolate complexes [17] e.g. the ethylenglycol complex at 1792 cm^{-1} and 1680 cm^{-1}. It is therefore likely that the surface hydroxyl ligands will substitute the benzonitrile ligands but not the pyridine ligands in the reacting complex. Even reaction of the non-phosphitated polymer according to eq. 2 resulted in a green polymer with the same IR-frequencies in the NO-region. Obviously reaction with the benzonitrile complex as well as the bridge splitting reaction leads to the same type of surface compounds.

However, reaction of the phosphitated polymer independent of the method used resulted in green-yellow polymers with NO-stretching frequencies at 1787 cm^{-1} and 1668 cm^{-1}. These frequencies are lower than those observed for the non-phosphitated polymers, more in agreement with those observed for phosphine complexes [11]. From our spectra we can however not exclude the presence of small amounts alcolate complexes even on the phosphitated polymer.

We have also studied the Mo-Cl stretching frequencies of our preparations. In all of them a band was present, which can be assigned to a Mo-Cl vibration. No significant differences in the position of this band (308 cm^{-1}) for preparation A-D was found but the intensity was markedly increased for preparations C and D compared to that of A and B. Two explanations are plausible viz. the presence of oligomeric chloro bridged complexes or a trans-chloro arrangement at Mo. Both

explanations are equally possible, if literature data [11,18] on Mo-Cl stretching frequencies and intensities are taken into account. On the basis of the stability of the different preparations under catalytic testing, vide, supra the oligomeric type of complexes are however the most likely ones.

A complete mapping of the type of complexes and their relative amount on the polymers is, however, a difficult task.

Olefin metathesis studies

The prepared polymer bound complexes were tested with respect to activity for the metathesis of Z-2-pentene.

As shown by Hughes [20] the type of complexes under discussion are activated by reaction with $EtAlCl_2$ and maximum activity was, in that study, found at a Al/Mo ratio of 5-6. We have also used the same co--catalyst but found that a much higher amount of co-catalyst was needed to reach the highest activity. The activity was strongly dependent on the amount of co-catalyst added (fig. 2) and maximum activity was found at about 7 mmol $EtAlCl_2$ per gram of polymer. This number corresponds to a Al/Mo ratio of 36 (preparation D). This high value of the Al/Mo ratio is not mainly due to the activation of the molybdenum complex, but is merely an effect of reactions of $EtAlCl_2$ with the polymer carrier. In figure 1 two types of functional groups in the polymer, which can react with $EtAlCl_2$, are recognized viz. hydroxylgroups -OH and carbonyl groups C=O. In addition also uncomplexed phosphite groups $-O-PPh_2$ are present on the polymer as shown by the Mo/P ratio (Table 1). As a result of these groups the three different $EtAlCl_2$ consuming reaction shown in eq. 4-6 are possible.

After reaction of the polymer with $EtAlCl_2$ the formation of ethane was observed by GLC-analysis, while the formation of ester carbonyl adducts (eq. 6) was detected by infrared spectroscopy in the carbonyl stretching region. Upon reaction of the catalyst with $EtAlCl_2$ the original CO-band of the polymer at 1728 cm^{-1} was split into a doublet containing the original band and a new one at 1632 cm^{-1} (fig. 3). The shift observed 96 cm^{-1} is in resemblance to that observed earlier [19] for $MeAlCl_2$-ester adducts (Δcm^{-1} = 98-126) or the shift we have observed (vide supra) for $EtAlCl_2$-methylstearate adduct (Δcm^{-1} = 126).

Instead of using $EtAlCl_2$ to block the Lewis basic groups in the polymer we have also used combinations of $AlCl_3$ and $EtAlCl_2$ in the activation procedure. $AlCl_3$ was not itself able to activate the catalyst. By the addition of $AlCl_3$ to the polymer (6 mmol/ g polymer) before the addition of $EtAlCl_2$ it was possible to reduce the amount of $EtAlCl_2$ needed to reach full activity by 47 %. This supports that the main consumption of $EtAlCl_2$ is due to reaction with the Lewis basic groups on the polymer.

As noted in the introductory paragraph Lewis basic groups in the polymer could eventually interact and diminish the catalytic activity of the Mo-catalyst. However, by blocking these sites via coordination or reaction with the co-catalyst their ability to interact with the catalytic center is substantially reduced, and thus catalytic activity will be maintained. Blocking of Lewis basic groups with a Lewis acidic co-catalyst could perhaps be used to tackle the problem of metathesis of functionalized olefines. We have in the present study made some efforts in that direction by investigating the metathesis of Z-2-pentene in the presence of methylstearate using the homogeneous $Mo(NO)_2(PPh_3)_2Cl_2/EtAlCl_2$ catalyst.

Initially we studied the complex formation between methylstearate and $EtAlCl_2$ by infrared measurements (ν (CO) methylstearate 1738 cm^{-1} and adduct 1611 cm^{-1}) and then also the catalytic activity for Z-2-pentene metathesis as a function of the C_{EtAlCl_2}/C_{ester} ratio (fig. 4). One can note the activity of the metathesis is low for conditions when the complex formation is low i.e. there are large quantities of free ester that can poison the catalytic system. When the main part of the ester groups are bonded in a complex with the Lewis acid, however, the activity rises sharply. The curve in figure 4 shows striking similarities to that of the polymer bound system in figure 2. In both cases a relatively large amount of $EtAlCl_2$ has to be used to reach maximum activity, because of the Lewis bases present.

Besides in the consumption of co-catalyst one other deverging behaviour of our polymer bound catalyst was observed. This is a lack of pretreatment period - time between addition of co-catalysed and olefin - needed to reach full activity. Hughes [20] found that a pretreatment period of 60 minutes gave the best initial activity for the homogeneous system. In our case the activity as depicted in figure 5 was found to be equally high, on simultaneous addition of catalyst, co-catalyst and olefin, as that observed for the analogous homogenous complex $Mo(NO)_2(PPh_2OBu)_2Cl_2$ after 60 minutes pretreatment.

The results presented in figure 5 shows that the two systems are equally active. With respect to the stereoselectivity at 0 % conversion, using the method described by Basset [21] to determine this quantity, the heterogenized system is also very similar to the analogous homogeneous systems. For our preparations (A-D) the

E/Z 2-butene ratio fall in the range of 0.22-0.26. Thus in very close resemblance to the value of 0.20-0.24 for homogeneous systems [22].

One object of the present study was to compare the mutual activity of our preparations. For all of them nearly the same activities, expressed as initial rate, were found, however.

The stability of these heterogenized complexes i.e. their tendency to metal-leaching is of interest for two reasons. Firstly, if they should be of any practical value it is essential that the stay intact. At any reasonable concentration of $EtAlCl_2$ (up to 7 mmol $EtAlCl_2$ / gram polymer) all of them (A-D) were stable as determined by AAS of the reactant solutions. At high concentrations (> 7 mmol $EtAlCl_2$/gram polymer) some leaching was observed for C and D. The reason for this is most likely the presence of halide bridged complexes, in these two preparations, of the type discussed in the previous section.

Secondly, the question wheter the ligand L stays co-ordinated to the active specie under the catalytic cycle is not yet solved. Since we have observed no metal-leaching from our polymers under catalytic operation this is indicative of an active intermediate with the ligand L co-ordinated to the metal, contrary to the active intermediate proposed by Seyferth [10].

The present study shows that highly polar polymers can be used as carriers for metal complexes active as metathesis catalysts, if a proper method of preparation is used. This study is also one of the very few existing examples in which a successful immobilization

has been done without altering the catalytic behaviour of the system i.e. where the activity and selectivity are essentially maintained.

Acknowledgment

Financial support from AB Karlshamns oljefabrik and the Royal Swedish Academy of Sciences are grafefully acknowledged.

References

1 J. Lieto, D. Milstein, R.L. Albright, J.V. Minkiewicz and B.C. Gates, CHEMTECH (1983) 46

2 F.R. Hartley and P.N. Vezey, Adv. Organometal. Chem. 15 (1977) 189

3 S. Warwel and P. Bushmeyer, Angew. Chem. 90 (1978) 131

4 S. Tamagaki, R.J. Card and D.C. Neckars, J. Am. Chem. Soc. 100 (1978) 6635

5 A. Uchida and M. Ko-Ori, J. Mol. Catal. 28 (1985) 209

6 R.H. Grubbs, S. Swetnick and S.C.H. Su, J. Mol. Catal. 3 (1977/78) 11

7 E.A. Zuech, W.B. Hughes, D.H. Kubicek and E.T. Kittleman, J. Am. Chem. Soc. 92 (1970) 528.

8 M. Leconte, Y. Ben Tarit, J.L. Bilhou and J.M. Basset, J. Mol. Catal. 8 (1980) 263

9 W.B. Hughes in Adv. Chem. Ser. 132 (1974) 192 Eds. D. Forster and J.F. Roth

10 K. Seyferth and R. Taube, J. Mol. Catal. 28 (1985) 53

11 F.A. Cotton and B.F.G. Johnson, Inorg. Chem. 3 (1964) 1609

12 C. Andersson and R. Larsson, J. Am. Oil Chem. Soc. 58 (1981) 675

13 W.R. Sorenson and T.W. Campbell, Preparative Methods in Polymer Chemistry, Interscience Publishers, 2nd ed. 1968, p. 155

14 M. Berglund, C. Andersson and R. Larsson, J. Organomet. Chem. 258 (1983) 195

15 C. Stubbe, W.M. LeSuer and G.R. Norman, J. Am. Chem. Soc. 77 (1955) 3526

16 A. Kemula and R.T. Iwamoto, J. Phys. Chem. 72 (1968) 1334

17 L. Bencze, J. Kohan and B. Mohai, Acta Chim. Hung. 113 (1983) 183

18 S. Sarkar and P. Subramanian, Inorg. Chim. Acta 35 (1979) L 357

19 S. Pasynkiewicz and K. Starowieyski, Ann. Soc. Chim. Pol. 41 (1967) 1139

20 W.B. Hughes, J. Am. Chem. Soc. 92 (1970) 532

21 J.L. Bilhou, J.M. Basset, R. Mutin and W.F. Graydon, J. Am. Chem. Soc. 99 (1977) 4083

22 N. Taghizadeh, F. Quignard, M. Leconte, J.M. Basset, G. Larroche, J.P. Laval and A. Lattes, J. Mol. Catal. 15 (1982) 219

Table 1 Analytical data

Preparation	Method	% Mo	% P	$\frac{\text{mol P}}{\text{mol Mo}}$[c]	$\frac{\text{mol N}}{\text{mol Mo}}$
A	1[a]	1.10	0.35	6.7	2.2
B	1[b]	1.20	0.21	5.8	1.8
C	2	1.20	0.36	5.8	2.0
D	2	1.84	0.55	3.7	2.0

a) L = pyridine

b) L = benzonitrile

c) Calculated from analysis of starting polymer and corrected for the weight increase based on molybdenum content.

Figure legends.

Fig 1. The copolymer of hydroxyethylmethacrylate and ethylendimethacrylate.

Fig 2. The initial rate R_{In} vs the amount of $EtAlCl_2$ (mmol/g polymer). Reaction conditions: 0.18 g catalyst, preparation A, olefin/Mo = 400, t = 23°C.

Fig 3. Infrared spectrum of the phosphitated polymer after reaction with $EtAlCl_2$ (7 mmol/g polymer).

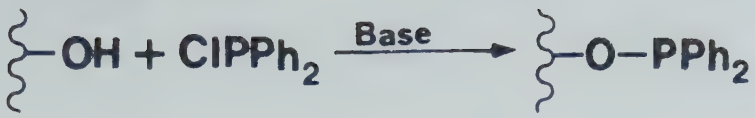
Fig 4. □ The percentage complex bound methylstearate (%CMS) as a function of the C_{EtAlCl_2} / C_{Ester} ratio as determined by infrared spectroscopic studies in chlorobenzene solution at 23°C.

▽ The initial rate (R_{In}) for the metathesis of Z-2-pentene with $Mo(NO)_2(PPh_3)_2Cl_2$ in the presence of methylstearate vs C_{EtAlCl_2} / C_{Ester}. Reaction conditions: C_{Cat} = 1.7mM, Olefin/Mo = 175, ester/Mo = 39, t= 23°C.

Fig 5. The metathesis of Z-2-pentene.
Reaction conditions: t = 23°C, Mo/olefin = 400

○ Catalyst: Preparation D, 0.072g, 7.3 mmol $EtAlCl_2$/g polymer.

● Catalyst: $Mo(NO)_2(PPh_2OBu)_2Cl_2$, C_{Cat} = 1.52mM, Al/Mo = 6.

eq.1 

eq.2 $$\left[Mo(NO)_2Cl_2\right]_n + 2nL \longrightarrow n\,Mo(NO)_2L_2Cl_2$$

eq.3 $$Mo(NO)_2L_2Cl_2 + 2L' \rightleftharpoons Mo(NO)_2L'_2Cl_2 + 2L$$

eq.4 $$-CH_2CH_2-OH + EtAlCl_2 \longrightarrow -CH_2CH_2-OAlCl_2 + \text{Ethane}$$

eq.5 $$-CH_2CH_2-OPPh_2 + EtAlCl_2 \rightleftharpoons -CH_2CH_2-OPPh_2{\cdot}AlEtCl_2$$

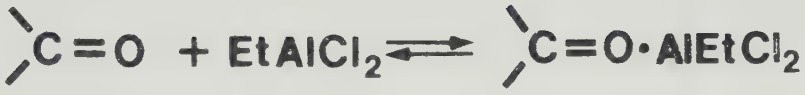
eq.6 

FIG.1

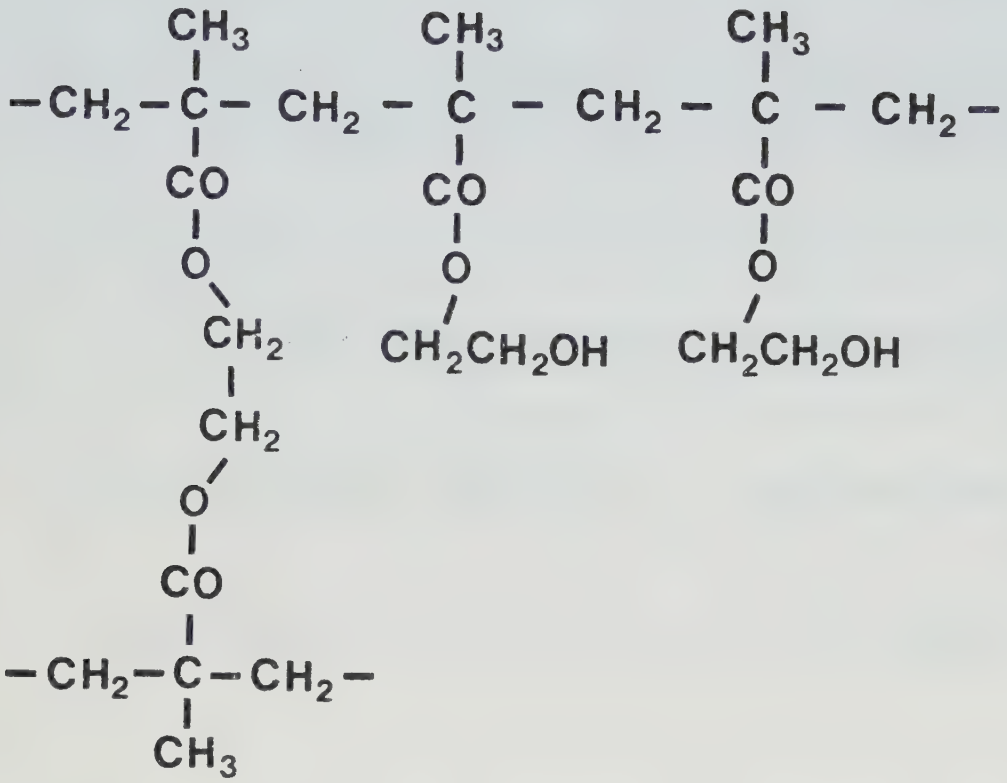

CH3
CH2 C CH2
CO
O
CH2
CH2
O
CO
CH2 C CH2
CH3
CH2 C CH2
CO
O
CH2CH2OH
CH2 C CH2
CO
O
CH2CH2OH

FIG.2

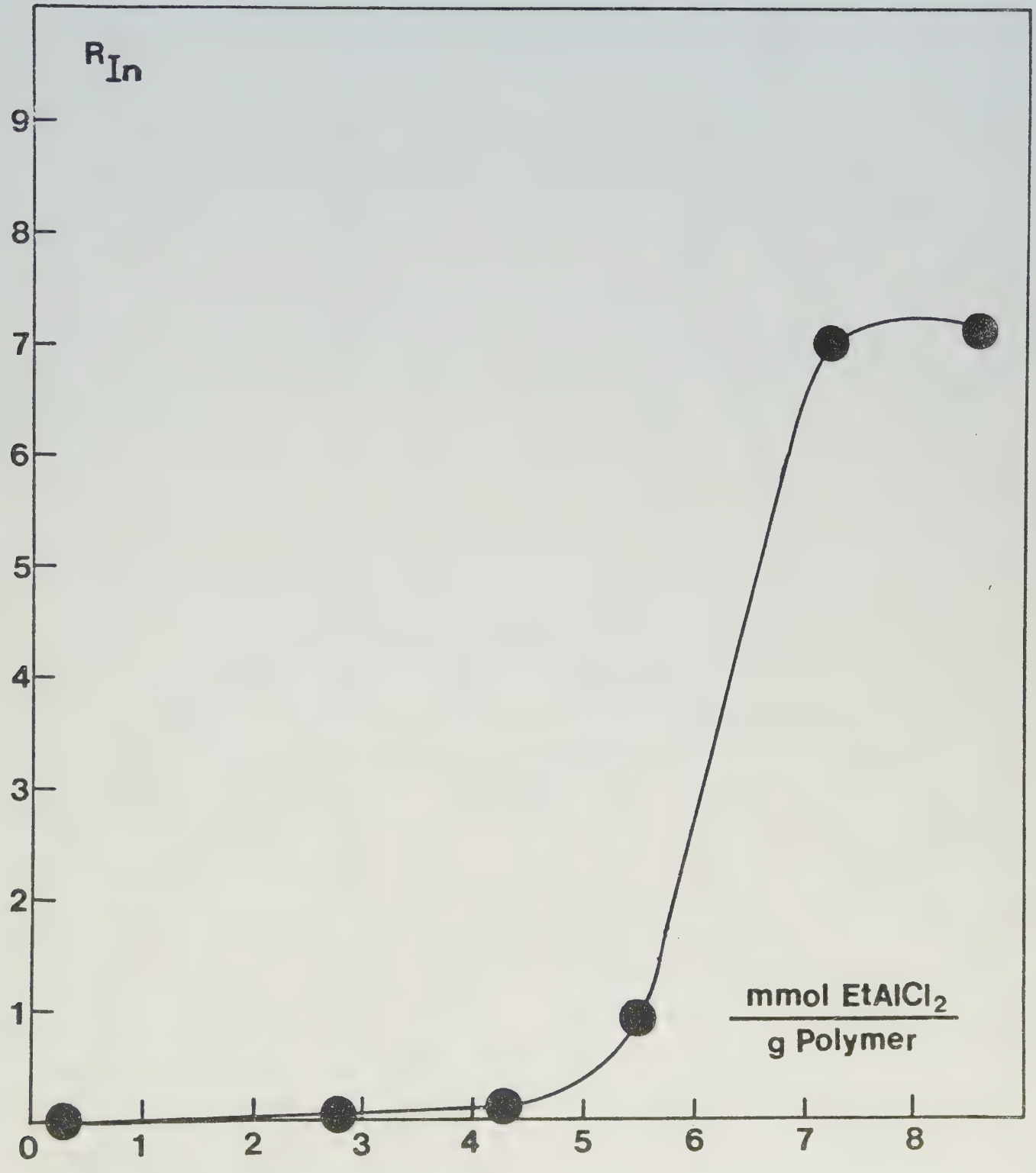


FIG.3

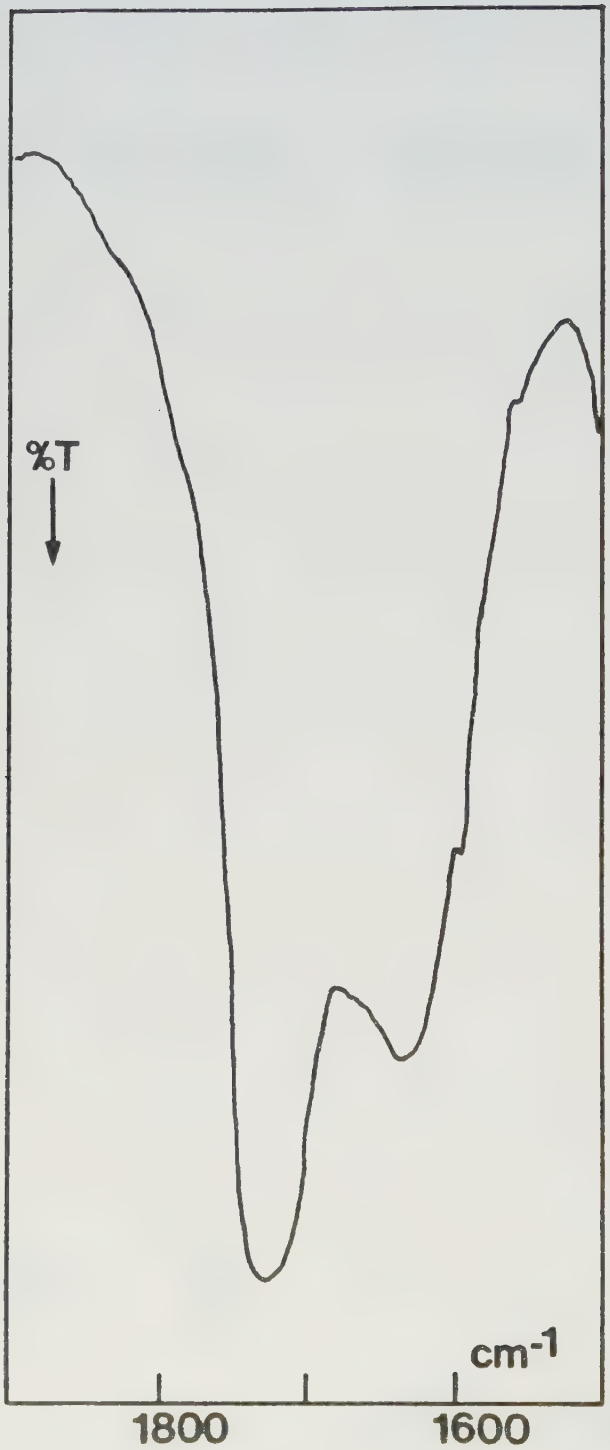


FIG.4

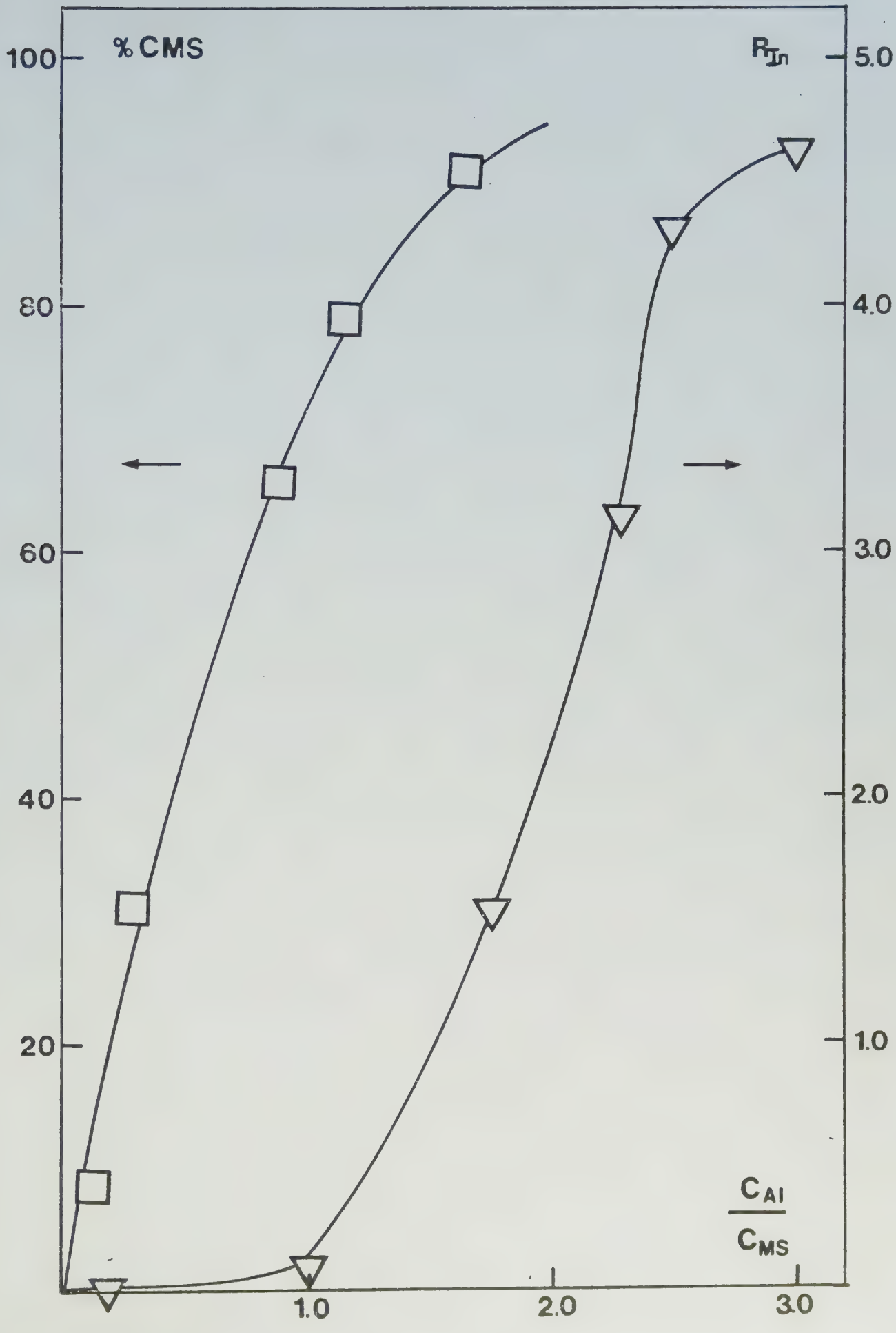
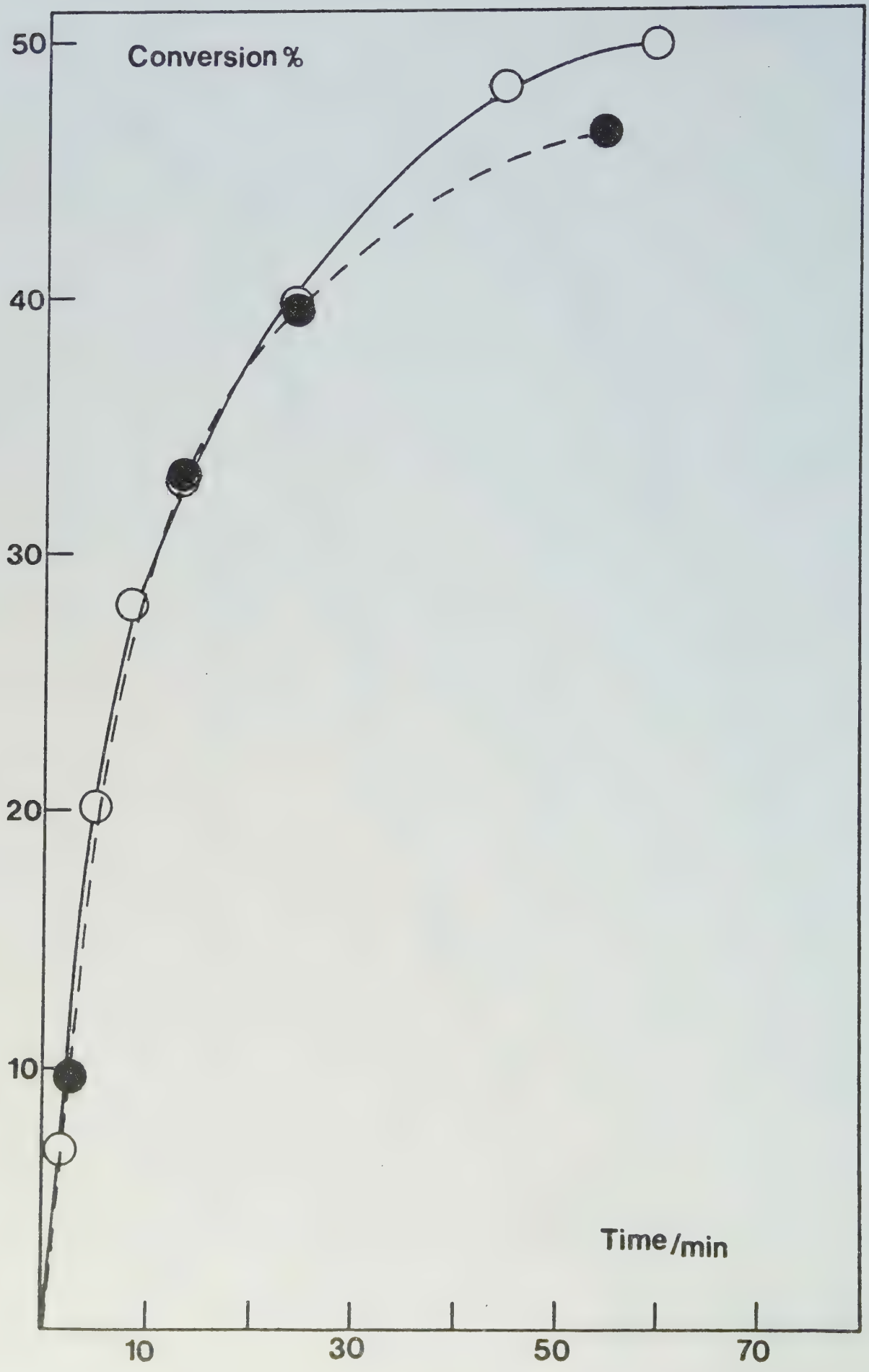


FIG.5



IV

Journal of Organometallic Chemistry, 292 (1985) C15—C17
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

OLEFIN METATHESIS OF ALKENYLTRIMETHYLSILANES

MATS BERGLUND, CARLAXEL ANDERSSON and RAGNAR LARSSON

Research group on catalysis, Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 124, S-221 00 Lund (Sweden)

(Received May 30th, 1985)

Summary

WCl_6 has been used as a catalyst for the metathesis of various alkenylsilanes and the degree of conversion found to be dependent on the distance between the olefinic bond and the silyl group. The first observation of metathetical conversion of allyltrimethylsilane in the absence of a co-catalyst is reported.

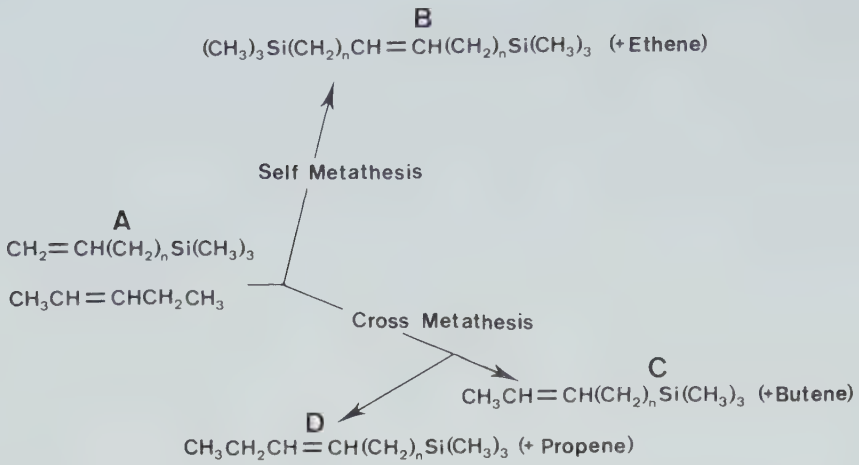
Several studies of metathesis of functionalized olefins, e.g. esters [1], ethers [2], amines [3] have been described. By means of such metathesis these substrates can be converted into difunctionalized olefins or, via cross-reaction with other olefins, into shorter or longer homologues [4].

Only few reports have dealt with metathetical conversions of alkenylsilanes. Friedman et al. [5] reported that vinyl- and allyl-trimethylsilane could be disproportionated, with low conversion, on a heterogeneous alumina-supported molybdenum catalyst. Recently Marciniec et al. described the successful metathetical conversion of vinyltriethoxysilane into 1,2-bis(triethoxy)-silylethene with phosphineruthenium complexes as catalysts [6]. We now report the first study of the use of WCl_6 as catalyst for disproportionation of vinyl-, allyl- and 3-butenyl-trimethylsilane, involving self-metathesis as well as co-metathesis. Reactions were carried out under nitrogen in a closed glass vessel at 25°C in chlorobenzene.

The following order of addition of the reactants was used. To the reaction vessel, filled with nitrogen, 1 ml of a stock solution of WCl_6 in chlorobenzene was added. Subsequently 10 ml of chlorobenzene, the cocatalyst and the substrate were added sequentially.

The cross-metathesis experiments were performed with *cis*-2-pentene as the second olefin. Two different alkenylsilanes are possible as a result of cross-reaction (**C** and **D**, Scheme 1); the self metathesis produces **B**. The cross-metathesis results are shown in Table 1.

0022-328X/85/$03.30 © 1985 Elsevier Sequoia S.A.



SCHEME 1. Products expected for the cross-metathesis of alkenyltrimethylsilanes (n = 0, 1, 2) and *cis*-2-pentene.

TABLE 1

CROSS-METATHESIS OF ALKENYLSILANES WITH 2-PENTENE

Entry	Catalytic [c] system	Sn/W	n	Conversion [a] of A (%)	Yield [b] C + D	C/D	Yield [b] B
1	$WCl_6/SnMe_4$	4	0	<1	—	—	—
2	WCl_6	—	0	4.3	0	—	0
3	$WCl_6/SnMe_4$	4	1	24.0	22.8	5.5	0.5
4	WCl_6	—	1	43.1	37.2	2.7	1.2
5	$WCl_6/SnMe_4$	4	2	44.1	35.3	4.9	3.9
6	WCl_6	—	2	8.0	5.1	—	0

[a] By GC. Column: 10% OV 17 on Chromosorb WHP. [b] In mol %. [c] $c_{WCl_6} = 1.05 \times 10^{-2}$ M, solvent: chlorobenzene; t 25°C; [A]/[Pentene] = 1, [A]/[WCl_6] = 50; reaction time: 20 h.

With vinyltrimethylsilane no metathetical conversion was observed (entry 1 and 2). Even addition of small amounts of vinyltrimethylsilane, e.g. 2 mole per mole WCl_6, totally inhibited the metathesis of *cis*-2-pentene with $WCl_6/SnMe_4$. This is in agreement with the results reported by Dolgoplosk et al. [7]. When, however, allyltrimethylsilane was used as a substrate reasonable yields of cross-products (C and D) were obtained with the usual $WCl_6/SnMe_4$ system as well as with the cocatalyst-free system. Apparently allyltrimethylsilane can itself activate WCl_6 to form an active catalyst. The first step in this activation is most probably an allylation of WCl_6, as indicated by the formation of 2.2—2.5 mol chlorotrimethylsilane per mole WCl_6. In contrast to allyltrimethylsilane, for which the most active system is the one without cocatalyst, 3-butenyltrimethylsilane reacts most effectively in the presence of $SnMe_4$ (entry 5 and 6); this is probably due to the weaker alkylating properties of 3-butenyltrimethylsilane compared to those of allyltrimethylsilane [8]. The self-metathesis results shown in Table 2 show that the distance between the double bond and the trimethylsilyl group is an important factor, the yield

TABLE 2

SELF-METATHESIS OF ALKENYLSILANES

Entry	Catalytic system	Sn/W	n	Yield of B [a] (%)	Selectivity (%)
7	WCl_6/4 EtAc/$SnBu_4$	4	0	0	—
8	WCl_6/4 EtAc/$SnBu_4$	4	1	2.2	96
9	WCl_6	—	1	4.2	95
10	WCl_6/4 EtAc/$SnBu_4$	4	2	20.0	94
11	WCl_6/$SnMe_4$	4	2	4.5	>95
12	WCl_6	—	2	<1.0	—

[a] In mol%.

of B increasing as this distance increases (entry 7, 8, 10). The same feature is also observed in the cross experiments for the WCl_6/$SnMe_4$ system (entry 1, 3 and 5, Table 1). The low overall conversion in the self-metathesis reaction is not surprising, since it is well known that WCl_6-based systems are not very effective for conversion of terminal olefins [9].

We also studied the synthetic utility of the cross-reaction by bringing allyltrimethylsilane into reaction with *cis*-2-butene; a yield of 76% (as indicated by GLC) of 2-butenyltrimethylsilane was achieved by passing a stream of *cis*-2-butene gas through the reaction vessel, so shifting the equilibrium by removal of the propene gas formed.

Contrary to earlier reports [1], our results indicate that the behaviour of silicon-containing olefins in the metathesis reaction is similar to that of other functionalized olefins. For instance, there is a dependence of the ease of reaction on the distance between the double bond and the functional group, just as in the case of ethers [2].

Acknowledgements. Financial support from the Royal Physiographic society is gratefully acknowledged.

References

1 J.C. Mol, J. Mol. Cat., 15 (1982) 35.
2 W. Ast, G. Rheinwald and R. Kerber, Rec. Trav. Chim. Pays-Bas., 96 (1977) M127.
3 C. Edwige, A. Lattes, J.P. Laval, R. Mutin, J.M. Basset and R. Nouguier, J. Mol. Cat., 8 (1980) 297.
4 J. Otton, Y. Colleuille and J. Varagnat, J. Mol. Cat., 8 (1980) 313.
5 R.A. Friedman, S.M. Nosakova, Yu.B. Kryokov, A.N. Bashirov, N.S. Nametkin and V.M. Vdovin, Izv. Akad. Nauk SSSR, Ser Khim., 20 (1971) 2100.
6 B. Mareiniec and J. Gulinski, IVth Intern. Symp. Homogeneous Catalysis, Leningrad, Sept. 24—28, 1984, Abstract no L8-1.
7 B.A. Dolgoplosk, J. Mol. Cat., 15 (1982) 193.
8 I.S. Akhrem, D.V. Avetisyan, R.S. Vartanyan, K.G. Shakhatuni and M.E. Volpin, Izv. Akad. Nauk. SSSR, Ser. Khim., 10 (1975) 2327.
9 K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983, Chapter 2 and 5.

V

Olefin metathesis of alkenylsilanes

Part II. On the initiation of olefin metathesis with organosilanes

Mats Berglund, Carlaxel Andersson and Ragnar Larsson

Research group of catalysis, Inorganic Chemistry 1,
Chemical Center, University of Lund, P.O.B. 124,
S-221 00 LUND, Sweden

Running title: Olefin metathesis of silanes

Proof and correspondence to

Mats Berglund
Research group of catalysis, Inorganic Chemistry 1,
Chemical Center, University of Lund, P.O.B. 124,
S-221 00 LUND, Sweden

Abstract.

The cross-metathesis of alkenylsilanes $CH_2=CH-(CH_2)_n-SiX_3$ n=1,2; X= CH_3,Cl,OMe with Z-2-pentene have been studied using WCl_6 as the catalyst precursor. For allyltrimethylsilane (ATMS, n=1, X=CH_3) the reaction proceeds without added co-catalyst but with an induction period. The catalytically active intermediat is in this case formed by allylgroup-transfer from Si to W as observed by the formation of $ClSiMe_3$. Allyltrichlorosilane and allyltrimethoxysilane requires the addition of an alkylating co-catalyst e.g. $SnMe_4$. The effect of addition of Lewis acid e.g. $AlCl_3$ or $AlBr_3$ show that for ATMS, the induction period is completely reduced and the activity substancially increased. The initial activity and the E/Z-stereoselectivity responds very similar to the addition of Lewis acid. The results indicate that the Lewis acid infer in the initiating, propagating and in the terminating step of the reaction.

INTRODUCTION

Since the pioneering study in 1972 by van Dam et.al. [1] on the metathesis of functionalized olefins, e.g. methyloleate this field has attained a considerable interest. The reason for this is that such reactions can give a range of different products, e.g. mono or difunctionalized olefins. These products can be of great synthetic and economic value [2,3]. So far only a few systems viz. $WCl_6/SnMe_4$ [1,4] and Re_2O_7/Al_2O_3 [5,6] have proven to be efficient catalysts for the metathesis of functionalized olefins. The difficulty lies in the deactivating effect of the polar substituents, which probably blocks the coordination sites of the catalyst. Adding to this list a recent paper [7] reports that properly designed metal carbenes can be used as catalysts for the above mentioned reactions.

One type of functionalized olefins which has been little studied is alkenylsilanes [8,9]. Alkenylsilanes has become increasingly important reagents in organic synthesis [10]. Therefore metathesis of silyl olefins might well develop to an important tool in the synthesis of organic rare and fine chemicals. With this in mind we have begun a study of suitable catalysts for this reaction. Another useful application of metathesis of organosilanes has been demonstrated by Streck [8] who synthezised polyalkenamers terminated with reactive silylgroups. By this method highly cross-linked polymers were obtained.

In most of the catalytic systems described above a co-catalyst is needed to activate the catalyst precursor. In the crossmetathesis of allyltrimethylsilane and Z-2-pentene [11] and also in the

ring-opening polymerization of cyclic olefins [12] it has been found that alkenylsilanes can, however, act as catalyst activators.

Three main routes to create an active catalyst from WCl_6 can be distinguished: i) treatment with alkylating agents [13], ii) reaction with hydride donors [14] or iii) electrochemical generation [15]. In a previous communication [11] we have suggested that the activating power of allyltrimethylsilane is due to its ability to act as a mild alkylating agent, i.e. it belongs to cathegory i). In the present paper we report further studies on the activation of WCl_6 with organosilanes and also on the metathetical conversion of different alkenylsilanes. As a model reaction we have chosen the cross-metathesis of Z-2-pentene and some selected alkenylsilanes, since such conditions are known [6] to be a more sensitive indication of activity than selfmetathesis.

EXPERIMENTAL

Chemicals

WCl_6 was purified by vacuum sublimation. Analytical grade chlorobenzene was dried over CaH_2 and distilled under nitrogen before use. Z-2-pentene (Fluka), tetramethyltin (Fluka) and allyltrimethylsilane (Jansen Chimica) were distilled and stored over molecular sieves under nitrogen. Allyltrichlorosilane [17], allyltrimethoxysilane [18] and 3-butenyltrimethylsilane [19] were prepared according to reported procedures. $AlBr_3$ and $AlCl_3$ (Jansen Chimica) were used as received and dissolved in chlorobenzene to the desired concentration. All catalytic manipulations were done under a oxygen-free nitrogen atmosphere.

Analysis

The reaction mixtures from the olefin methathesis experiments were analyzed on a Perkin Elmer F17 GC equipped with a computing integrator (LCI-100). Two different columns were used viz. 10 % OV-17 on Chromosorb WHP and 10 % SE-30 on Chromosorb WHP. The different products obtained were identified by mass spectrometry and by comparision of their retention times with that of authentic samples. Relative response factors were determined for authentic samples or in some cases calculated according to the method of Scanlon and Willis [16].

Olefin methathesis experiments

The metathesis experiments were carried out in a stirred glass vessel at room temperature as descriebed previously [11,20]. The following general conditions were used: Solvent: Chlorobenzene $C_{WCl_6} = 1.0 \times 10^{-2}$ M, $C_{Z\text{-}2\text{-}pentene} = C_{alkenylsilane} = 0.5$ M. Samples were quenched with pyridine except in those cases when chlorotrimetylsilance were to be analyzed.

The term cross products given in the figure legends is defined as the sume of the products $CH_3CH = CH(CH_2)_nSiX_3$ and $CH_3CH_2CH = CH(CH_2)_nSiX_3$.

RESULTS AND DISCUSSION

I Catalyst activation

The presently accepted mechanism of the metathesis reaction involves the initial formation of a metalcarbene complex. This carbene can be formed from traditional alkylating agents, e.g.

SnR_4, BuLi or Et $AlCl_2$ by the sussesive alkyl groups transfer to the metal followed by an α-hydrogen elimination [21].

In an catalytic system free from an alkylating co-catalyst the substrate itself must be able to initiate the carbene formation. For tetraorgano substituted silanes the capacity for transfer of the organic group to WCl_6 has been found to depend on the nature of this group [22]. E.g. reaction of R_4Si and R_3SiPh with WCl_6 has been found to give 16 % and 63 % conversion respectively at equimolar metal to silane ratio. Furthermore in the latter case it was the Si-Ph bond that was predominantly broken. The low reactivity of tetraalkylsilanes has also been demonstrated in metathesis experiments [23]. Allyltrimethylsilane (ATMS), on the other hand, is more prone to undergo Si-C bond cleavage, as observed in the reaction with WCl_6 [24] and with Pd(II) and Hg(II) salts [25]. In the latter case stable π-allyl complexes of Pd^{2+} and Hg^{2+} could be isolated. For WCl_6, however, only chlorotrimethylsilane and decomposition products as propene and 1,5 hexadiene have been observed. These are most likely derived from an intermedial tungsten allyl complex.

As pointed out in the introduction ATMS has a dual role under cross-metathesis conditions: It acts both as a co-catalyst, generating the active catalyst, and as a substrate. In the activity plot of Fig. 1 (Al/W = 0) an induction period of 5 minutes can be observed. Since we have observed that premixing of WCl_6 and ATMS, for 5 minutes before the addition of Z-2-pentene, result in the immediate formation of cross products the induction period most likely reflects the time needed to produce the initial carbene.

From the results presented in figures 1-3 it is clear that the induction period is also affected by the addition of Lewis acids, e.g. AlX_3 (X = Cl, Br) and Lewis bases, e.g. diethylether. Independent of whether $AlBr_3$ or $AlCl_3$ was used the qualitative picture was the same. Even at a very low Al/W ratio no induction period was observed (Figs. 1, 3). Addition of diethylether to the system resulted in an increased induction period, more so with increasing ether concentration (Fig. 2). This effects of Lewis bases and acids can be explained if we assume, in analogy to the reaction between Pd^{2+} or Hg^{2+}, that the formation of a W-π-olefin complex is the initial step in a reaction sequence leading to the active carben (Eq. 1).

By abstracting a chloroligand from WCl_6 the Lewis acid creates a stronger electrofile viz. WCl_5^+. Hence the conditions for olefin coordination is improved. The Lewis base on the other hand has quite the opposite effect. It competes with the silylolefin for the coordination site of the metal. This competition is, of course, expected to be more pronounced with increasing ether concentration.

The decrease of the induction period on AlX_3 treatment can, however, also be related to the formation of an allyl-Al compound in the reaction system. In this way a stronger alkylating agent is present, which is more prone to react with tungsten (equations 2-4). An analogous intermediate has been claimed to exist in the redistribution equilibria of benzyltrimethylsilane catalyzed by $AlCl_3$ [26].

The Lewis acid might in certain cases be bound to the metal-atom via halide bridges, which can facilitate the formation of a carbene [27]. This is yet another way be which the presence of AlX_3 can decrease the induction period.

The initiation was in all cases followed by a formation of $ClSiMe_3$ as given in Table 1. Two conclusions can be drawn from the data of Table 1. First, since WCl_6 is the only source of chlorine the degree of chloro ligand transfer from WCl_6 to Si is reflected in the amount of $ClSiMe_3$ formed on the initiation. This reaches a limiting value of 3.4 equivalents at an Al/W ratio of 0.4. Secondly, since no formation of $BrSiMe_3$ was detected reaction 4 must be included in the total reaction scheme.

The process of generating the active intermedial from WCl_6 is generally believed to involve a reduction to a WCl_4 species [28] as a first step. The reduction can be achieved by the successive transfer of two alkyl groups from an alkylating co-catalyst and subsequent reductive elimination of the organic groups as exemplified for PhC ≡ CNa [29], BuLi [28, 31] or $EtAlCl_2$ [30]. In this process chloride ions are released from WCl_6 to form, in the above examples, NaCl, LiCl or $AlCl_3$. Hence in the case of ATMS as an activator two equivalents of $ClSiMe_3$ is expected to form in the reduction of W(VI) to W(IV), together with products such as propen and 1,5-hexadiene.

A comparison of our data for initial activity (Figs. 1 and 3) with those of the amount of $ClSiMe_3$ formed (Table 1) reveals that there is a close resemblance. When the amount of $ClSiMe_3$ increases, indicating an increased allyl-group transfer, the initial activity increases. This demonstrates that allyl-group transfer beyond the two equivalents needed to reduce W(VI) to W(IV) is necessary to generate the active catalyst. In a calorimetric study of the system $WCl_6/EtAlCl_2$ [30] a Al:W ratio of 4 was found to give a tungsten species which strongly interacts with the added olefin, e.g. cyclohexene, but the question as to the optimum level of the

tungsten: co-catalyst ratio is still a matter of controversy [30]. It is most likely that the conversion of WCl_6 into active carbene is not stoichiometric. Competing side reactions in the carbene generating step will most likely reduce the amount of tungsten that is converted into active carben [21]. The relative amount of $ClSiMe_3$ (3.4 eq/WCl_6) formed at maximum rate can therefore not be interpreted as the actual amount of ATMS needed to generate an active carbene from WCl_6. Such a statement can only be justified if the total amount of active carbene is known.

II Catalytic activity

Lewis acidity or basicity have also a great influence on the catalytic activity (Figs. 1-3). This can be expressed as the initial rate or as the total yield. The initial activity measured as the initial slope of the activity curves increased slightly at an Al/W ratio of 0.2 compared to the case without Al (Fig. 1). At an Al/W ratio of 0.4 a drastic increase in the initial activity was found and for Al/W ratios in the range 0.4 - 2.0 it remained essentially the same. This holds for $AlBr_3$ (Fig. 1) and for $AlCl_3$ (Fig. 3). Addition of ethylether to the system on the other hand (Fig. 2) resulted in a decreased initial activity, more so with increasing concentration of ether.

From the results presented in figures 1 and 3 we conclude that a minimum amount of AlX_3, in the range of 0.4 equivalents compared to W, is needed in order to reach, what seems to be the limiting value of the initial rate of our system. Moreover, the total yield

is also substancially affected by the addition of AlX_3. If the Lewis acidity of the system is increased beyond a certain level, either by increasing the concentration of AlX_3 or by changing from $AlBr_3$ to $AlCl_3$ this resulted in a lowering of the total yield, e.g. compare Al/W = 0.6 to Al/W = 1.0 of figure 1 or the curves of figures 1 and 3 at similiar Al/W-ratios.

The lowered yield of metathesis products at high Lewis acidity can have different reasons. Competing side reactions such as e.g. allylation of the chlorobenzene solvent, consumes ATMS and hence lower the yield of cross products. In our system we have in fact observed that the selectivity to metathesis products decreases at high Al/W ratios (Table 1).

The amount of Friedel-Craft products found is, however, not large enough to explain the very drastic change in the yield, from 50 % at Al/W = 0.6 to 20 % at Al/W = 1.0. We therefore suggest that the lowered yield is caused by a reduced lifetime of the catalytic system at high Lewis acidity. By this the benefical effect of the Lewis acid on the initial rate is offset by its longterm poisonous effect.

The increase in the initial reaction rate that we have observed on addition of AlX_3 to the system can have two different origins, which might operate separatly or consecutively: i) As indicated by the formation of increased amounts of $ClSiMe_3$ the total amount of active carbenes probably increases on addition of AlX_3 to the system; ii) Via halide ion abstraction from the carbene complex AlX_3 can create a vacant coordination site at the carbene-complex (eq. 5) In this way the conditions for olefin coordination is

improved. If olefin coordination is the rate determing step, an increased reaction rate should result on addition of AlX_3 to the system as observed. Kress and Osborn [32], have found that a cationic carben can indeed be the propagating carbene in the metathesis of Z-2-pentene. This carben was formed by the reaction of a Lewis acid, e.g. $GaBr_3$ with $W(CHR)(OCH_2R)_2Cl_2$.

III E/Z Stereo-selectivity

Besides the catalytic activity an other essential property pertaining to a metathesis catalyst is the E/Z stereo-selectivity. Even for this property our system is very sensitive to addition of Lewis acid. This is shown for one of the cross-products, viz. 2-butenyltrimethylsilane in figure 4. Since the E/Z ratio at zero percent conversion is much larger with $AlBr_3$ or $AlCl_3$ added, the Lewis acid must be involved in propagating step (vide infra). Increase of the Lewis basicity of the system by the addition of diethyleter, does not alter the stereoselectivity (Fig. 4). This observation suggests that, contrary to AlX_3, ether does not interfere in the propagating step [7].

For AlX_3 the E/Z ratio was found to reach a limiting value of 0.5 (Table 1) at a Al/W ratio of 0.4, independent of further AlX_3 addition. This is very similar to the sharp sudden increase in the initial reaction rate at the same Al/W ratio (vide supra).

Several suggestions to explain how the Lewis acid influences the E/Z-stereoselectivity have been published [33, 34, 35]. Basset et.al. [33] proposed that the Lewis acid induced "electronic changes in the coordination sphere of the tungsten atom". These changes should infer a modification in the relative stability of

the different metallacyklobutane intermediats that are supposed to be possible intermediates. As another explanation Katz [34] has suggested that the Lewis acid interact by clearing the carbon-metal bond in the metallacycle. In that way a metallapropyl cation is formed with free rotation of the bonds.

Basing our conclusion on the very close resemblance observed between the initial activity and the E/Z stereoselectivity, table 1, we conclude that the propagating carbene complex is greatly modified by the Lewis acid. Perhaps to an extreme where a cationic tungsten carbene is formed.

IV Metathesis of Z-pentene initiated by ATMS

We have also studied the metathesis of Z-2-pentene using WCl_6 as the catalyst precursor and ATMS only acting as a co-catalyst. We have found that similarly to the case of the cross-metathesis experiments (Figs. 1 and 3) the addition of Lewis acid decreases the induction period and increases the initial rate. One might for instance compare curves A and C or curves B and D of figure 5. Additionally we noted that the self-metathesis activity is dependent on the ATMS/W ratio, e.g. compare curves A and B or curves C and D of figure 5. Maximal activity in terms of either initial rate or conversion was found at a ATMS/W ratio of 4 (curve D in figure 5). At higher ratios the cross-metathesis became important and hence a lower yield of Z-2-penten self-metathesis products was found.

V Metathesis of alkenylsilanes other than ATMS

From our results presented up to this point of the present paper and also previously [11] it seems likely that the key requirement for the activation of WCl_6 with alkenylsilanes is that the olefinic bond is in the position β to Si. It is known [36] that in a series of alkenylsilanes $R_3Si(CH_2)_n CH = CH_2$ the reactivity in ionic additions, e.g. $(SCN)_2$ is in the following order $n = 1 >> 2 > 0$. The exceptionally high reactivity of allylsilanes in such reactions is usually attributed to the influence of the silicon atom on the β-carbon atom collectively called the β-effect for which several factors are responsible. This can be expressed as a high electron donating power of the R_3SiCH_2-group exemplified in the review by Jarvie [36]. By replacement of the alkyl groups on the silicon by electronegative substituents the +I effect is reduced, which leads to a lower reactivity in ionic addition reactions [36]. From the above arguments and to further substanciate how the β-effect influences in the activation of WCl_6 with alkenylsilanes we have studied one case where the olefinic bond is placed γ to carbon viz. 3-butenyltrimethylsilane (BTMS) and two cases of allylsilanes with electronegative substituent at silicon viz. allyltrichlorosilane and allyltrimethoxysilane.

We have previously found [11] that the yield obtained on cross-metathesis of BTMS and Z-2-pentene in the absence of AlX_3 was only 5 % in 20 hours. This is substancially lower than the 40 % yield after 300 minutes obtained for ATMS (curve A Fig. 2). However, as was the case for ATMS, the reactivity of BTMS is, strongly affected by the addition of AlX_3 to the system, as shown in figure 6. The role of AlX_3 in the activation and in the propagating

step is most likely the same in both cases. It should be observed that the amount of Lewis acid needed to increase the reaction rate is markedly higher for BTMS than for ATMS. The low reactivity of BTMS is expected from the arguments discussed above. BTMS with the double bond in the γ-position should have a lower tendency for transferring the butenyl-group to tungsten. At high Al/W ratio the initial alkylation of W probably runs via an intermediate Al-alkyl resulting in a substancially more active system.

The involvement of the β-effect on the acivation of WCl_6 with alkenylsilanes is also nicely demonstrated in the case of allyltrichlorosilane and allyltrimethoxysilane. For both these alkenylsilanes no activity was found in the cross-metathesis with Z-2-pentane, most likely as an effect of the electron withdrawing substituents on silicon which decrease their reactivity toward tungsten. Alternatively these substrates with polar substituents can act as catalyst poisons and thereby block the reaction. To test this we have studied the metathesis of the two silanes with WCl_6 as the catalyst precursor and $SnMe_4$ as the co-catalyst. In these experiments the initiation does not rely on the initiating ability of the silanes themselves, they are merely substrate. For both substrates we found that they undergo metathetical conversion [Fig. 7], and allyltrichlorosilane gave ~45 % yield of cross-products within 120 min. A slow deactivation was found in the case of allytrimethoxysilane, which resulted in a limited yield of cross-products of around 15 %. To our opinion the results in figure 7 demonstrates that the potential poisoning effect of the polar substituents can not fully explain the total lack of catalytic activity in the absence of added co-catalyst.

We therefore conclude that ATMS has unique properties among alkenylsilanes to activate WCl_6 to an active metathesis catalyst. This property of ATMS is mot likely due to the β-effect. As soon as this β-effect is offset either by changing the position of the olefinic bond or by electronegative substituents on silicon the activating power is reduced or completly lost.

REFERENCES

[1] P.B. van Dam, M.C. Mittelmeijer and C. Boelhouver
J. Chem. Soc. Chem. Commun. (1972) 1221.

[2] C. Boelhouwer and J.C. Mol
J. Am. Oil. Soc. 61 (1984) 425

[3] J.C. Mol
J. Mol. Cat. 15 (1982) 35

[4] R.H. Bosma, A.P. Kouwenhoven and J.C. Mol
J. Chem. Soc. Chem. Commun. (1981) 1081

[5] R.H.A. Bosma, G.C.N. van den Aardweg and J.C. Mol
J. Organomet. Chem. 255 (1983) 159

[6] R.H.A. Bosma, G.C.N von den Aardweg and J.C. Mol
J. Organomet. Chem. 280 (1985) 115

[7] F. Quignard, M. Leconte and J.M. Basset
J. Chem. Soc. Chem. Commun. (1985) 1816

[8] R. Streck
J. Mol. Cat. 15 (1982) 3

[9] R.A. Friedman, S.M. Nosakova, Yu.B. Kryukov, A.N. Bashkirov, N.S. Nametkin and V.M. Vdovin
Izv. Akad. Nouk. SSSR Ser. Khim. 20 (1971) 2100

[10] Tilt Chan and I. Fleming
Synthesis (1979) 761

[11] M. Berglund, C. Andersson and R. Larsson
J. Organomet. Chem. 292 (1985) C 15

[12] I.A. Oreshkin, L.I. Red Kina, I.L. Kershenbaum, G.M. Chernenko, K.L. Makovetsky, I.L. Tinyakova and B.A. Dolgoplask
Europ. Polym. J. 13 (1977) 447

[13] K.J. Ivin
Olefin Metathesis, Academic Press, London, 1982, Chapter 2

[14] S.A. Matlin and P.G. Sammes
J. Chem. Soc. Perkin 1 (1978) 624

[15] M. Gilet, A. Mortreux, J. Folest and F. Petit
J. Am. Chem. Soc. 105 (1983) 3876

[16] J. Scanlon and D.E. Willis
J. Chrom Sci. 23 (1985) 333

[17] N. Furuya and T. Sukawa
J. Organomet. Chem. 96 (1975) C 1

[18] J. Pola, M. Jakoubkova and V. Chvalovsky
Collct. Czech. Chem. Commun. 43 (1978) 3391

[19] C.R. Hauser and C.R. Hance
J. Am. Chem. Soc. 74 (1952) 5092

[20] M. Berglund and C. Andersson
J. Mol. Cat., in press

[21] R.H. Grubbs in Comprehensiv. Org. metal. Chem.
Eds G. Wilkinson, F.G.A. Stone and E.W. Abel
Pergamon Press, 1982, Chapter 54.

[22] I.S.A. Khrem, D.V. Auetisyan, R.S. Vartanyan, K.G. Shakhatuni and M.E. Volpin
Izv. Akad. Nauk. SSSR, Ser. Khim. 24 (1975) 2327

[23] J. Levisalles, H. Rudler, D. Cuzin and T. Rull
J. Mol. Cat. 26 (1984) 231

[24] I.Ya Ostrovskaya, L.I. Redkina and K.L. Makovetsky
Izv. Akad. Nauk. SSSR, Ser. Khim. 29 (1980) 2650

[25] I. Haiduc and V. Popa
Avd. Org. metal. Chem. 15 (1977) 113

[26] D.H. O'Brien and T.J. Hairstone
Organometal. Chem. Rev. A 7 (1971) 95

[27] V. Dragutan, A.T. Balaban and M. Dimonie
Olefin metathesis and ring-opening polymerisation,
John Wiley and son, 1985, Chapter 6

[28] K. Ichikawa, T. Takagi and K. Fukuzumi
Transition Met. Chem. 1 (1976) 54

[29] K. Ichikawa, T. Takagi and K. Fukuzumi
Bull. Chem. Soc. Jpn 49 (1976) 750

[30] D.H. Singleton and D.J. Eatough
J. Mol. Cat. 8 (1980) 175

[31] I.-L. Wang, M.R. Merapace and M. Brown
J. Catal. 26 (1972) 455

[32] J. Kress and J.A. Osborn
J. Am. Chem. Soc. 105 (1983) 6346

[33] N. Taghizadeh, F. Quignard, M. Leconte, J.M. Basset,
J.P. Laval and A. Lattes
J. Mol. Cat. 15 (1982) 219

[34] T.J. Katz and W.H. Hersh
Tetrahedron. Lett. (1977) 585

[35] K.C. Ott, J.B. Lee and R.H. Grubbs
J. Am. Chem. Soc. 104 (1982) 2942

[36] A.W.P. Jarvie
Organometal. Chem. Rev. A 6 (1970) 153

Table 1

Effect of various $AlBr_3/WCl_6$ ratios on the cross-metathesis of allyltrimethylsilane and Z-2-pentene.

Al/W[a]	$ClSiMe_3/W$[a]	E/Z[b]	Yield of cross-products after 1 minute (%)	Selectivity[c] after 16 minutes (%)
0	2.1	0.3	0	96
0.2	2.9	0.4	1.5	94
0.4	3.4	0.5	14.0	94
0.6	3.4	0.5	14.4	94
1.0	3.2	0.5	15.0	91

a) molar ratio

b) see figure 4

c) selectivity = [ATMS] + [metathesis products]/C_{ATMS}

Figure legends

Figure 1

Effect of $AlBr_3$ addition.

The yield of crossproducts in the cross-metathesis of allyltrimethylsilane and Z-2-pentene vs. time at various $AlBr_3/WCl_6$ molar ratios.

Figure 2

Effect of diethylether addition.

The yield of crossproducts in the cross-metathesis of allyltrimethylsilane and Z-2-pentene vs. time
A: WCl_6, B: WCl_6+Et_2O, C: WCl_6+2Et_2O

Figure 3

Effect of $AlCl_3$ addition.

The yield of crossproducts in the cross-metathesis of allyltrimethylsilane and Z-2-pentene vs. time at various $AlCl_3/WCl_6$ molar ratios.

Figure 4

E/Z-2-butenyltrimethylsilane ratio vs. yield of cross--products in the cross-metathesis of allyltrimethylsilane and Z-2-pentene.
A: WCl_6, B: WCl_6+0.6 $AlCl_3$, C: WCl_6+0.6 $AlBr_3$, D: WCl_6+Et_2O

Figure 5

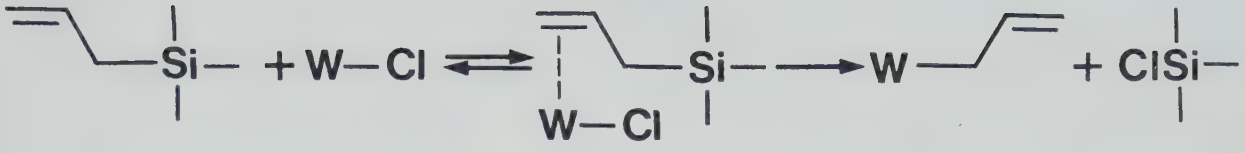
Metathesis of Z-2-pentene with the catalyst system WCl_6/ATMS/$AlBr_3$.
A: Al/W=0, ATMS/W=2; B: Al/W=0, ATMS/W=4; C: Al/W=0.4, ATMS/W=2
D: Al/W=0.4, ATMS/W=4

Figure 6

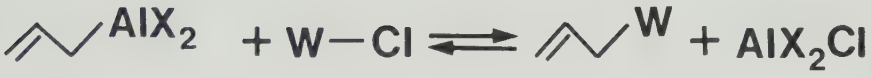
The yield of crossproducts in the cross-metathesis of 3-butenyltrimethylsilane and Z-2-pentene at various $AlBr_3/WCl_6$ molar ratios.

Figure 7

The yield of crossproducts in the cross-metathesis of Z-2-pentene and allyltrimethoxysilane (A) or allyltrichlorosilane (B) with the catalyst system WCl_6+2 $SnMe_4$.

eq.1 

eq.2

eq.3 

eq.4 $AlX_2Cl + XSiMe_3 \rightleftharpoons AlX_3 + ClSiMe_3$

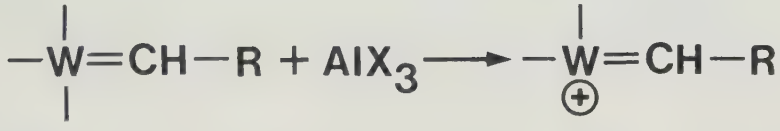
eq.5 

Fig.1

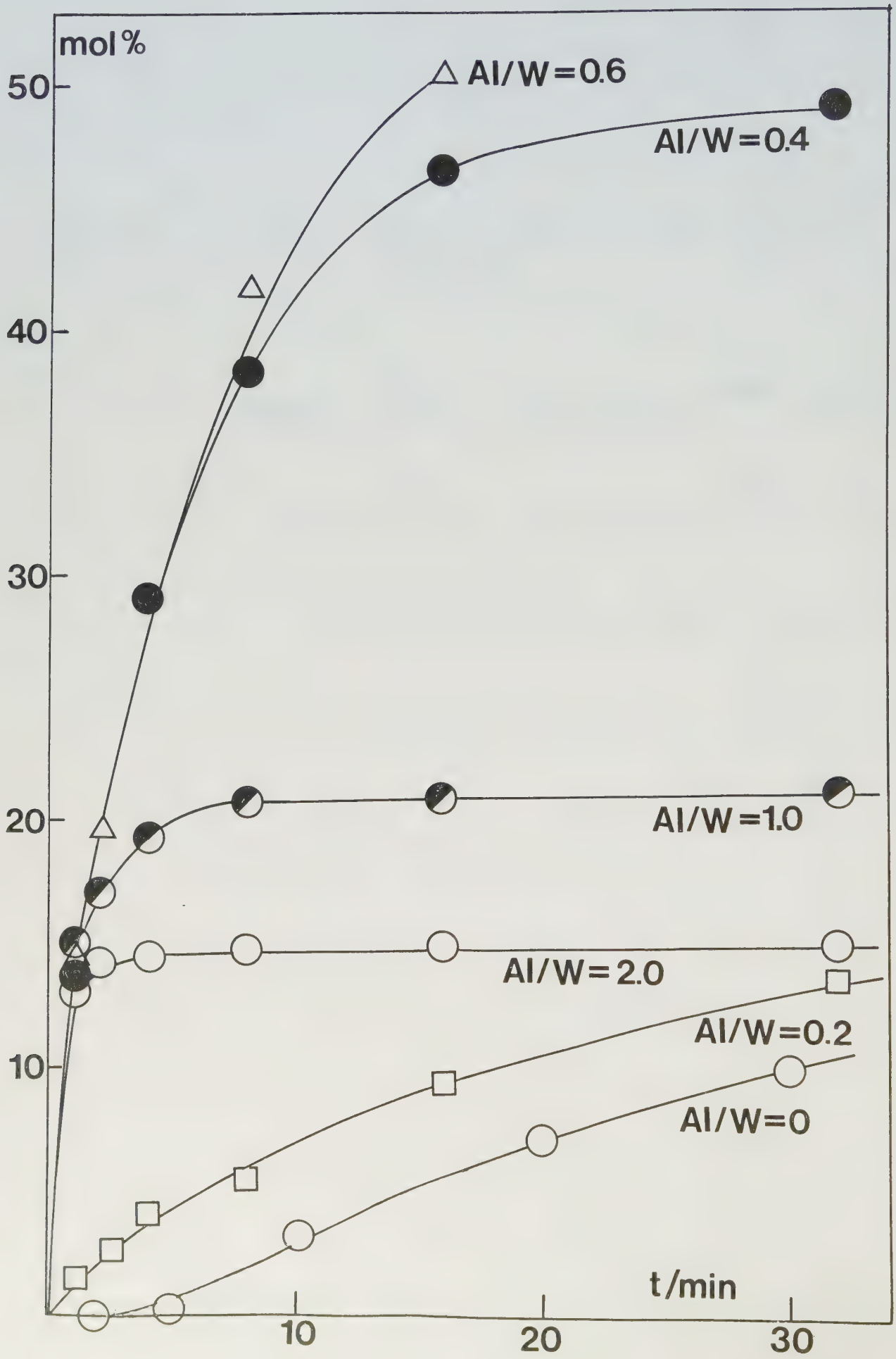

mol %
50
40
30
20
10
Al/W=0.6
Al/W=0.4
Al/W=1.0
Al/W=2.0
Al/W=0.2
Al/W=0
t/min
10
20
30

Fig.2

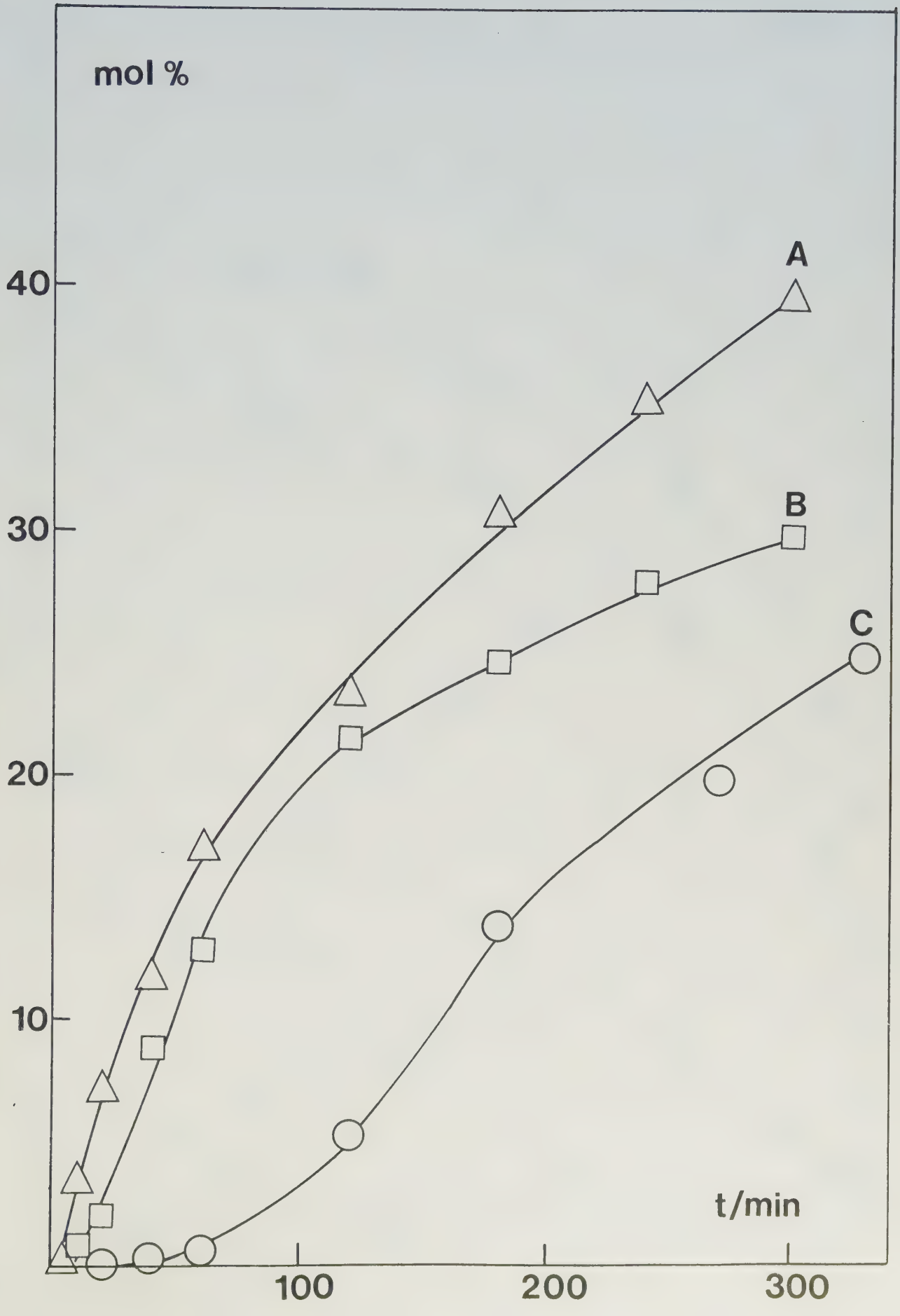


Fig.3

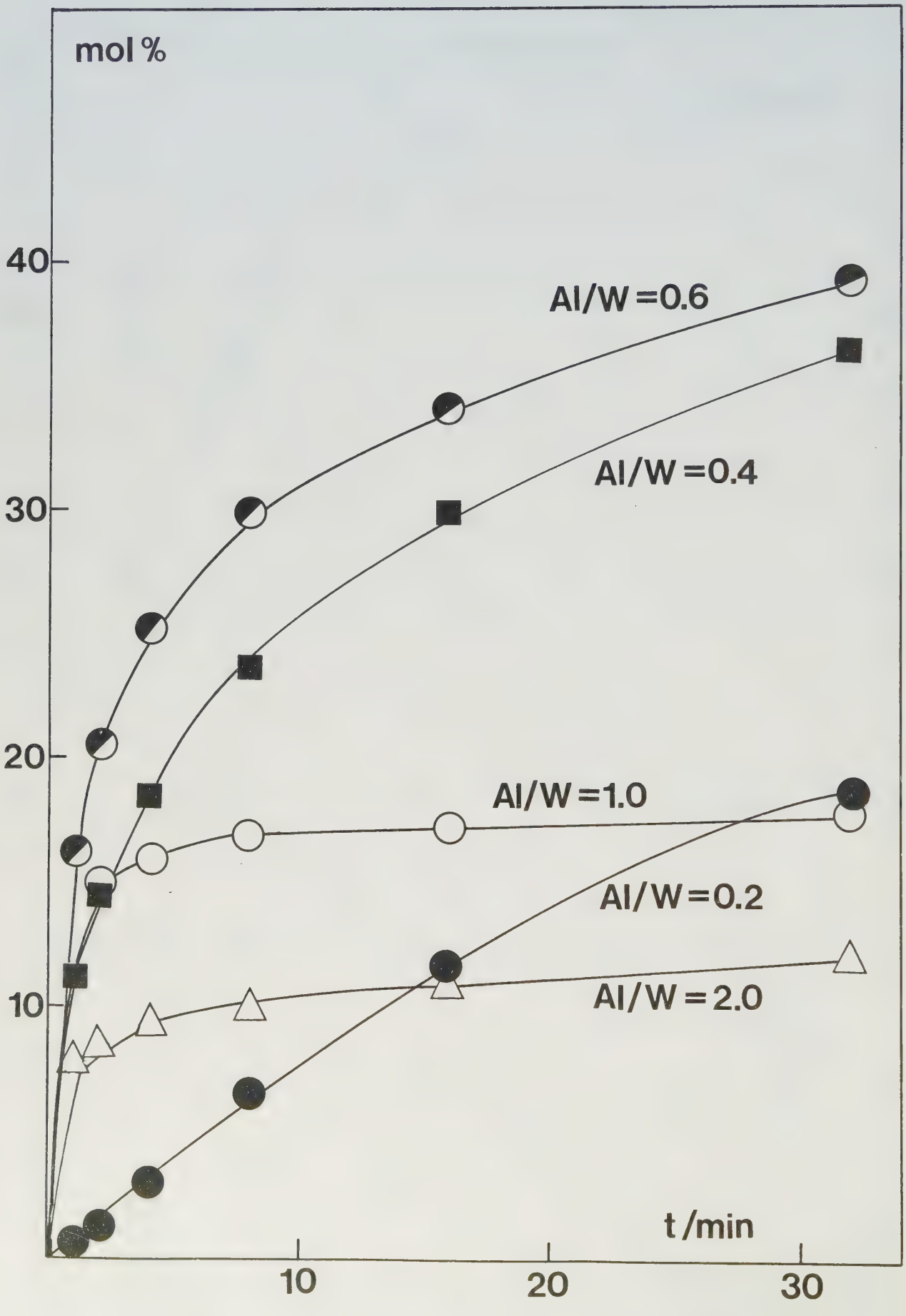


Fig.4

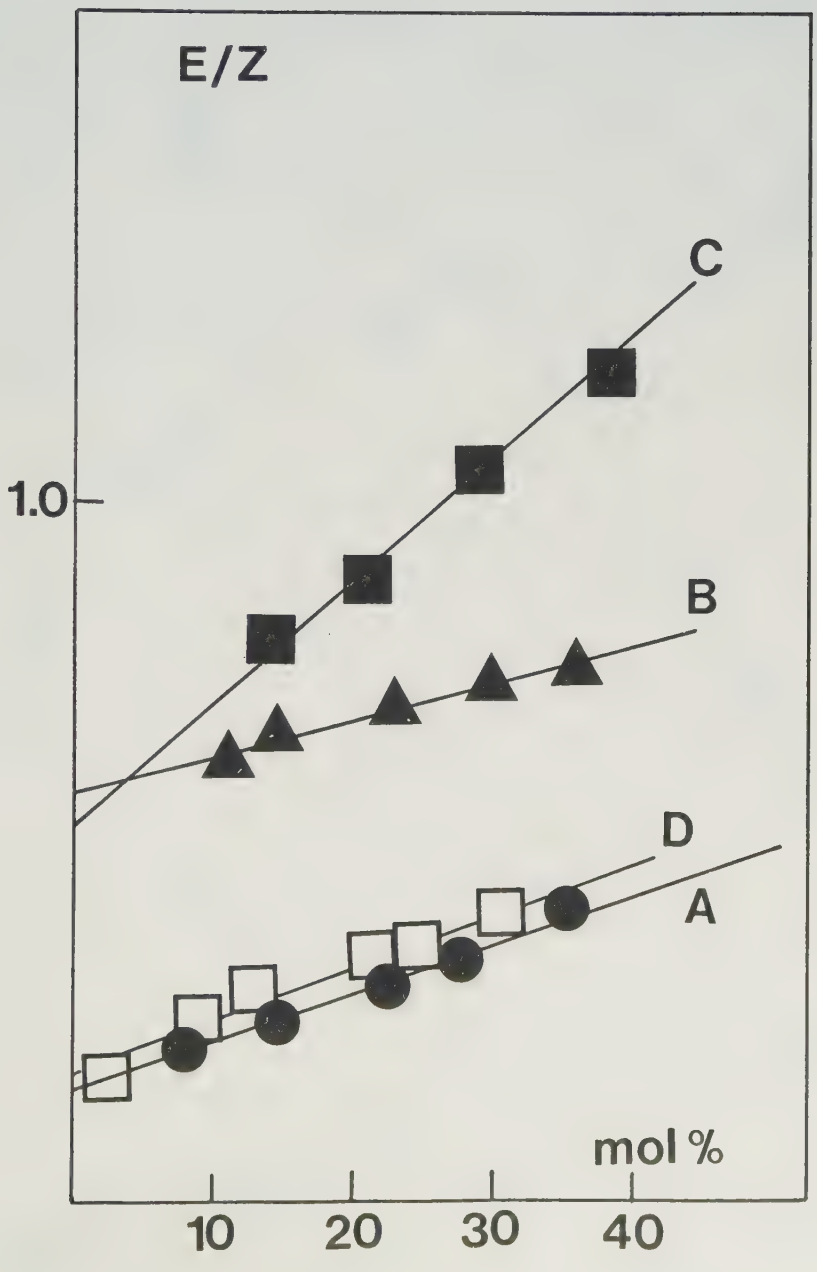


Fig.5

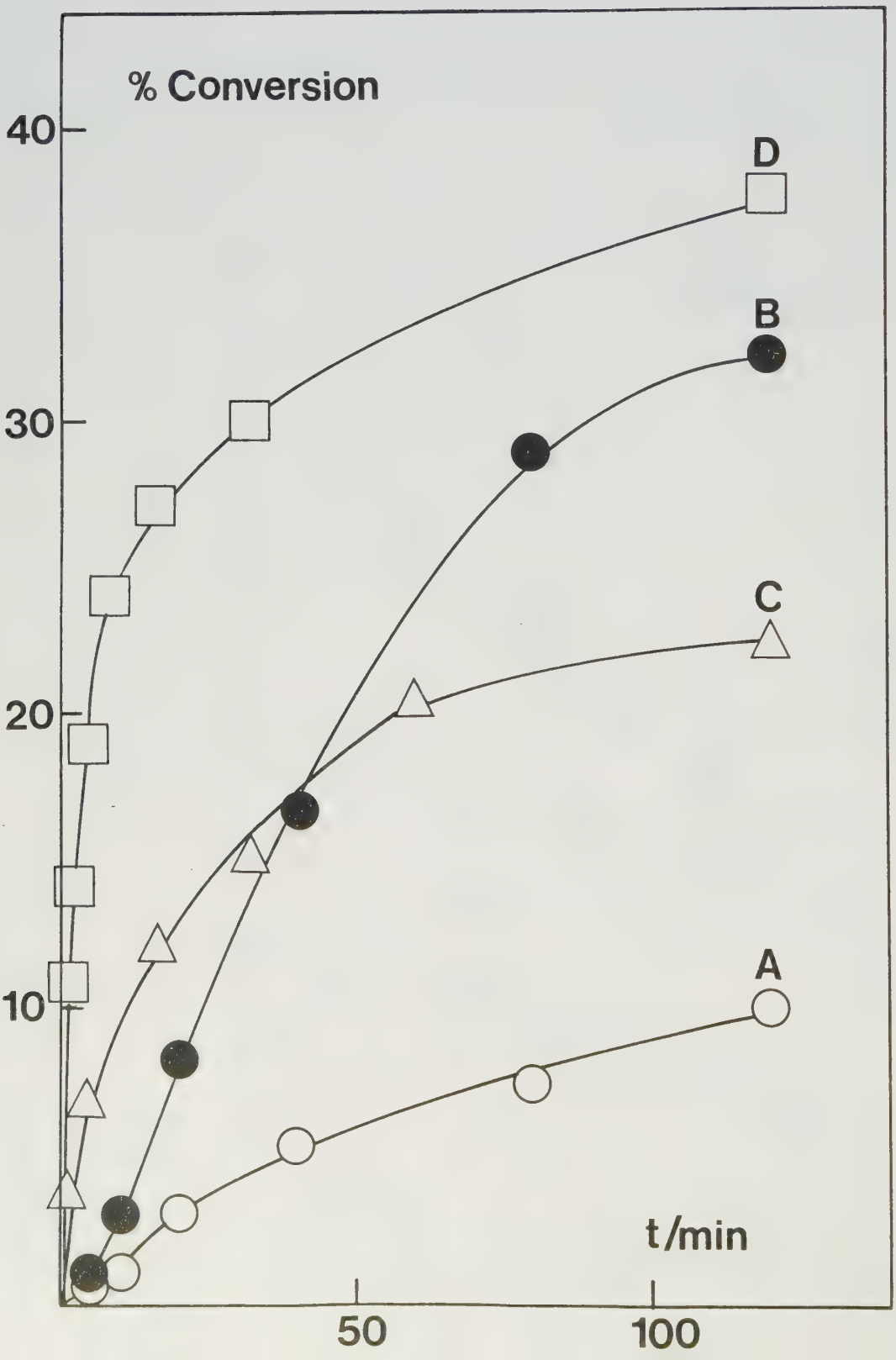


Fig.6

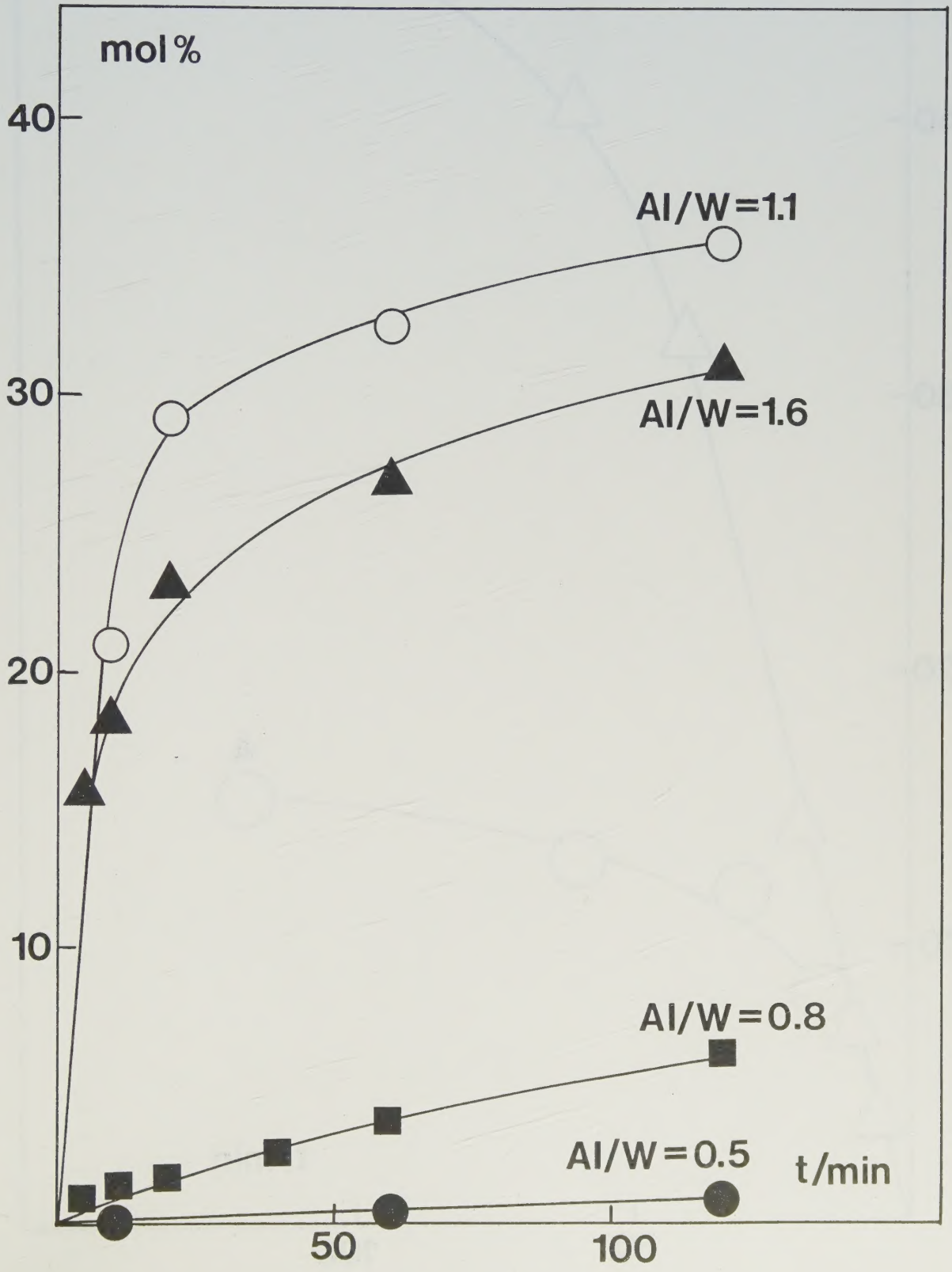


Fig.7